The Chemistry of Functionalized Silyl Anions(Dissertation_全文)

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Preface

The study presented in this thesis has been carried out under the direction of Professor Yoshihiko Ito at the Department of Synthetic Chemistry of Kyoto University during April, 1990 to October, 1993 and under the direction of Professor Kohei Tamao at Institute for Chemical Research of Kyoto University during November, 1993 to September, 1995. The study is concerned with the chemistry of functionalized silyl anions.

The author wishes to express his sincerest gratitude to Professor Yoshihiko Ito for his kind guidance, valuable suggestions, and encouragement throughout this work. The author is deeply grateful to Professor Kohei Tamao for his constant advice, valuable discussions, and encouragement during the course of the study. The author also wishes to express his gratitude to Associate Professor Masahiro Murakami, Associate Professor Akio Toshimitu, Dr. Masaya Sawamura, Dr. Yoshiki Nakagawa, Dr. Eiji Ihara, Dr. Michinori Suginome, Dr. Hitoshi Hamashima, Dr. Chitaru Hirosawa, Mr. Makoto Shiozaki, Mr. Yoshihiro Tarao, and Mr. Shigehiro Yamaguchi for their helpful suggestions and hearty encouragement. Thanks are also due to Dr. Yoshiki Nakagawa for his work of X-ray structural analysis and Dr. Hitoshi Hamashima for his help for the measurements of NMR spectra. The author also wishes to thanks to Messrs. Tatsuya Kobayashi, Yoko Tanaka, Akimitsu Okamoto, Hitoshi Ohtani, Noriyuki Doi, and other members of Prof. Ito's research group and Prof. Tamao's research group for their active collaborations.

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Contents

Part II

(Alkoxysilyl)lithiums

General Introduction

Carbanion chemistry plays a central role in the whole field of organic chemistry:[1] Most of a huge number of carbanions are functionalized carbanions stabilized by heteroatoms,[2] including α-heteroatom substituted carbanions **A**.

(A)

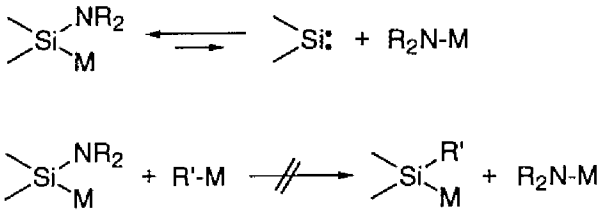
(B)

In contrast, silyl anions have been studied much less extensively than carbanions.[3,4] Synthetically useful silyl anions have long been limited only to several simple triorganosilyl anions such as Ph_3Si^-,[5,6] Ph_2MeSi^-,[6] $PhMe_2Si^-$,[6] Me_3Si^-,[7] and $(Me_3Si)_3Si^-$.[8] Furthermore, in the chemistry of functionalized silyl anions, Cl_3Si^-,[9] $(RO)_nMe_{3-n}Si^-$,[10] HPh_2Si^-,[11] $H(Mes)_2Si^-$,[12] and $(MesCO)(Me_3Si)_2Si^-$[13] have only been reported. The first two are postulated active species generated in situ in the presence of quenching agents and HPh_2Si^- is obtained in about 10% yields and tends to polymerize readily. Thus, virtually no stable α-heteroatom substituted silyl anions have been prepared.

In the light of these circumstances and the potential utility of functionalized silyl anions, the author has started to search stable and tractable functionalized silyl anions of type **B**.

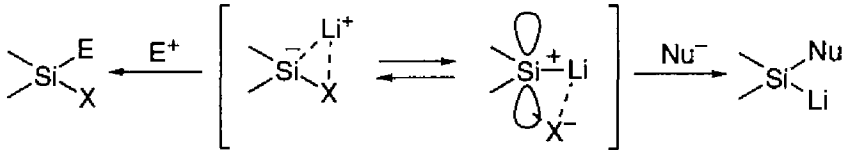
Amino groups ($X = NR_2$) were chosen as functional groups on silicon because of the high stability towards organometallic reagents;[14] it was thus anticipated that aminosilyl anions must be stable with respect to both intermolecular substitution and intramolecular α-elimination to silylene species (Scheme 1). It is noted here that some theoretical studies[4b,c] have predicted the comparable stability of two model systems MeH_2Si^- and $(H_2N)H_2Si^-$, as well as their much higher stability than the corresponding carbanions.

Scheme 1



Alkoxy groups (X = OR) were also chosen as functional group on silicon; it was anticipated that (alkoxysilyl)lithiums might behave as "silylenoids", analogous to carbenoids,[15] which exhibited both nucleophilic nature and electrophilic nature (Scheme 2). Silylenoids have been far less studied. To date only one theoretical study has been performed on a (lithium)(fluoro)silylenoid SiH_2LiF.[16] The result suggests that the Si-F bond is weakened when the electropositive lithium atom is attached to the silicon atom, resulting in the appearance of a positive charge on silicon. Some experimental reports have postulated silylenoids $R_2Si(X)M$ without evidence as reaction intermediates in reduction of dihalosilanes R_2SiX_2 with alkali metals M, especially in polysilane synthesis.[17] Reactivities of silylenoids, however, have never been investigated. Study on silylenoids may thus shed a new light also on the mechanism of the polysilane synthesis.

Scheme 2



Survey of This Thesis

This thesis describes the new chemistry of functionalized silyl anions, that is, (aminosilyl)lithiums and (alkoxysilyl)lithiums.

Part I deals with three (aminosilyl)lithiums, that is, $(Et_2N)Ph_2SiLi$, $(Et_2N)_2PhSiLi$, and $(Et_2N)PhMeSiLi$ and the related compounds.

Chapter 1 describes preparation and reaction of three [(amino)(phenyl)silyl]lithiums as the first members of stable functionalized silyl anions. Two methodologies have been examined: (1) Tin-lithium exchange reactions of (aminosilyl)stannnanes with *n*-butyllithium or *tert*-butyllithium, and (2) direct reaction of (amino)phenylchlorosilanes with lithium metal in THF. The (aminosilyl)lithiums undergo coupling with a variety of chlorosilanes to form the corresponding functionalized disilanes and trisilanes. The (aminosilyl)lithiums in solution are observable by ^{13}C, ^{29}Si, and ^{7}Li NMR spectroscopies.

Chapter 2 describes homocoupling reactions of amino- and diamino-alkylchlorosilanes with lithium metal in THF at room temperature to form the corresponding symmetrical diamino- and tetraaminoalkyldisilanes, respectively. They are transformed into chloro- and alkoxyalkyldisilanes under mild conditions.

Chapter 3 describes the reactivity control of aminosilyl anions. (Aminosilyl)(alkyl)magnesiums, which are prepared from (aminosilyl)lithiums and alkyl Grignard reagents, are useful silylating reagents for Si-Si bond elongation reactions. A competitive cleavage reaction of the Si-Si bond encountered with (aminosilyl)lithiums is suppressed. Synthesis of functionalized oligosilanes has been achieved by use of the magnesium reagents.

Chapter 4 describes synthetic applications of aminosilyl anions. An (aminosilyl)lithium, and the corresponding copper and magnesium reagents serve as a hydroxy anion equivalent through (1) allylic substitution, (2) addition to vinyloxirane, (3) addition to acetylene, and (4) conjugate addition (Michael addition), followed by oxidative cleavage of the silicon-carbon bonds. Highly regio- and stereoselective transformations have been achieved in all cases.

Chapter 5 describes UV absorption spectra of a series of (amino)(phenyl)disilanes, which have been interpreted in terms of the n - σ conjugation between the nonbonding electrons on nitrogens and the Si-Si σ-bonding electrons. X-ray crystal structure of a 1,1,2,2-tetraamino-1,2-diphenyldisilane has also been determined.

Part II deals with (alkoxysilyl)lithiums, (alkoxydisilanyl)lithiums, and (allyloxysilyl)lithiums.

Chapter 6 describes the first results of silylenoid chemistry, analogous to the carbenoid chemistry. (*tert*-Butoxysilyl)lithium (*t*-BuO)Ph_2SiLi can be prepared from (*tert*-butoxysilyl)stannane with *n*-butyllithium in THF and is stable at −78 °C. In the presence of 12-crown-4, this species is stable as silyl anion even at 0 °C and reacts with electrophiles only. In contrast to this, the (alkoxysilyl)lithium exhibits the ambiphilic reactivity and undergoes self-condensation smoothly at 0 °C to form (*t*-BuO)Ph_2Si-Ph_2SiLi or butylation in the presence of an excess amount of *n*-butyllithium and TMEDA to form (*n*-Bu)Ph_2SiLi. The ambiphilic reactivities could be accounted for by contribution of two extreme structures, that is, a nucleophilic silylenoid structure and an electrophilic silylenoid structure.

Chapter 7 describes reduction of alkoxy-, amino-, and hydrochlorosilanes with lithium 1-(dimethylamino)naphthalenide at low temperatures to give the corresponding alkoxy-, amino-, and hydrosilyllithiums, respectively. This method provides the first access to a (dialkoxysilyl)lithium. Electrophilicity of the (dialkoxysilyl)lithium extremely decreases in contrast to that of (monoalkoxysilyl)lithiums.

Chapter 8 describes reaction of a di(alkoxy)chlorosilane to give the (dialkoxysilyl)lithium selectively. In contrast, reaction of mono(alkoxy)chlorosilanes with lithium metal at 0 °C gives [2-(alkoxy)disilanyl]lithiums selectively via immediate self-condensation of the resulting (alkoxysilyl)lithiums. The [2-(alkoxy)disilanyl]lithiums undergo coupling with chlorosilane and 1,4-addition to an α,β-unsaturated ester.

Chapter 9 describes the first example of sila-Wittig rearrangement. (Allyloxysilyl)lithiums undergo [2,3]Wittig-type rearrangement smoothly to form lithium allylsilanolates. A crossover reaction supports the intramolecular rearrangement mechanism.

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Part I

(Aminosilyl)lithiums

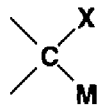
Chapter 1

The First Stable Functionalized Silyl Anions: (Aminosilyl)lithiums

Abstract: Three [(amino)(phenyl)silyl]lithiums were prepared as the first members of stable functionalized silyl anions. Two methodologies have been examined: (1) Tin-lithium exchange reactions of (aminosilyl)stannnanes with *n*-butyllithium or *tert*-butyllithium, and (2) direct reaction of (amino)chlorosilanes with lithium metal in THF. The latter procedure is more convenient and gives better yields. The (aminosilyl)lithiums are stable for 3 - 6 days without drop in activity. The (aminosilyl)lithiums undergo coupling with a variety of chlorosilanes to form the corresponding functionalized disilanes and trisilanes. The (aminosilyl)lithiums in solution are observable by ^{13}C, ^{29}Si, and ^{7}Li NMR spectroscopies.

Introduction

Carbanion chemistry plays a central role in the whole field of organic chemistry:[1] Most of a huge number of carbanions are functionalized carbanions stabilized by heteroatoms,[2] including α-heteroatom substituted carbanions (**A**). Reported herein are the initial results on the analogous species in silicon chemistry (**B**).



(A)

(B)

$(Et_2N)Ph_2SiLi$ **1**

$(Et_2N)_2PhSiLi$ **2**

$(Et_2N)MePhSiLi$ **3**

Silyl anions have been studied much less extensively than carbanions.[3,4] Synthetically useful silyl anions have long been limited only to several simple triorganosilyl anions such as Ph_3Si^-,[5,6] Ph_2MeSi^-,[6] $PhMe_2Si^-$,[6] Me_3Si^-,[7] and $(Me_3Si)_3Si^-$.[8] Although four functionalized silyl anions, Cl_3Si^-,[9] $(RO)_nMe_{3-n}Si^-$,[10] HPh_2Si^-,[11] and $H(Mes)_2Si^-$[12] have been reported, the first two are postulated active species generated in situ in the presence of quenching agents and HPh_2Si^- is obtained in about 10% yields and tends to polymerize readily. Thus, stable heteroatom substituted silyl anions have never been prepared.

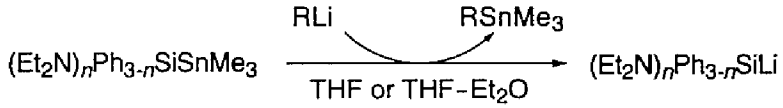
Amino groups (X = NR_2) were chosen as functional groups on silicon because of the high stability towards organometallic reagents;[13] it was thus anticipated that aminosilyl anions must be stable with respect to both intermolecular substitution and intramolecular α-elimination to silylene species. It is noted here that recent theoretical studies[4b,c] have predicted the comparable stability of two model systems MeH_2Si^- and $(H_2N)H_2Si^-$, as well as their much higher stability than the corresponding carbanions.

Results and Discussion

The author has now succeeded in preparation of three stable (amino)(phenyl)silyl anions **1** - **3**. Tin-lithium exchange reactions of (aminosilyl)stannanes with butyllithiums were first examined as the most promising route[14] (Scheme 1). The $(Et_2N)Ph_2Si$ derivative **4** indeed reacted smoothly with *n*-butyllithium at 0 °C within 30 min to give a greenish solution. Trapping with Me_3SiCl afforded the corresponding aminodisilane **6** in 90% yield, indicative of the formation of the (aminosilyl)lithium **1** in solution. Similarly, (diaminosilyl)lithium **2** was obtained from **5** and *tert*-butyllithium at -30 °C but in somewhat lower 77% yield: Trapping with Me_3SiCl afforded the corresponding aminodisilane **7**. These results prompted the author to examine the simple, standard method. Thus, the direct reaction of aminosilyl chlorides[15] **8** and **9** with lithium metal in THF set in at 0 °C to give immediately deep blue-green solutions; after 4 h, (aminosilyl)lithiums **1** and **2** were formed in quantitative yields (scheme 2). The reaction of **10** proceeded

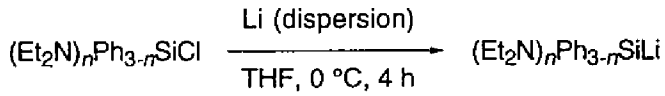
slowly to give the (aminosilyl)lithium **3** in 80% yield in 1 day at 0 °C: Trapping with Me_3SiCl afforded the corresponding aminodisilane **11**. Significantly, these (aminosilyl)lithiums are so stable as to be kept at 0°C under nitrogen for several days without noticeable drop in activity. Thus, the activity of **1** remained constant at 0 °C for 6 days and decreased to 78% after 14 days, and **2** and **3** were stable at least for 3 days; the (amino)(diphenyl)silyl anion **1** is more stable than the other (monophenyl)silyl anions **2** and **3**, in consonant with the stability order for the known (triorganosilyl)lithiums.

Scheme 1

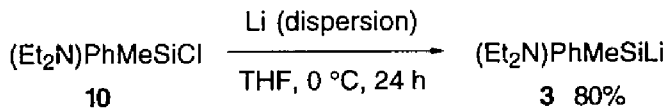


4 (n = 1): R = n-Bu, 0 °C, 0.5 h — **1** (n = 1) 90%
5 (n = 2): R = t-Bu, −30 °C, 4 h — **2** (n = 2) 77%

Scheme 2



8 (n = 1) — **1** (n = 1) 98%
9 (n = 2) — **2** (n = 2) 97%



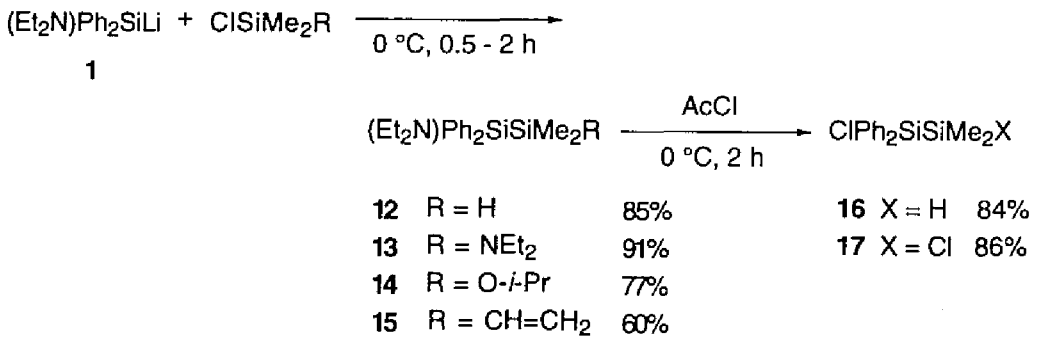
10 — **3** 80%

$(Et_2N)Ph_2SiSiMe_3$ **6** $(Et_2N)_2PhSiSiMe_3$ **7** $(Et_2N)PhMeSiSiMe_3$ **11**

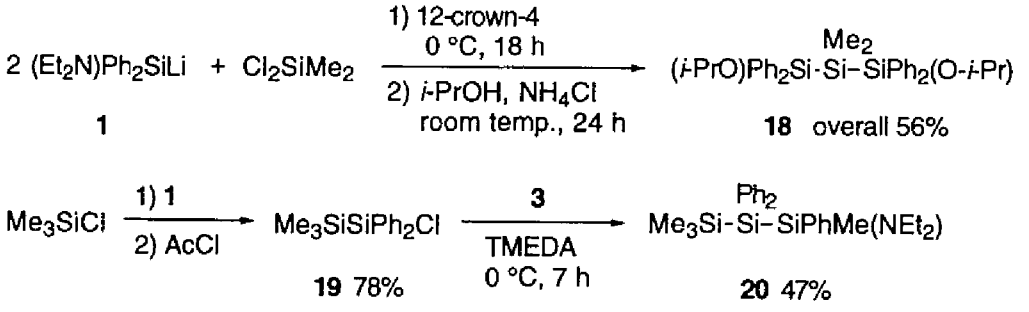
Versatility of the (aminosilyl)lithiums in organosilicon chemistry is apparent from some representative transformations shown in Scheme 3. Several points deserve comment. (1) All the (aminosilyl)lithiums **1** - **3** undergo coupling with a variety of chlorosilanes to form the corresponding disilanes **12** - **15**, most of which

are polyfunctionalized and unsymmetrical disilanes and hence hardly accessible by conventional methods. The Si-N bonds in the primary products can be converted into the Si-Cl bonds by just mixing with an acyl chloride such as acetyl chloride as exemplified by transformations from **12** - **13** to **16** - **17**, respectively. (2) A one-step introduction of two functional silyl groups into a dichlorosilane is possible as shown by the formation of dialkoxytrisilane **18**. (3) A stepwise Si-Si bond elongation can be achieved by sequential treatment of a chlorosilane with (aminosilyl)lithiums, as examplified by the formation of trisilane **20** which contains all three different silicon moieties. It is noted that all the functionalized disilanes and trisilanes prepared herein are structurally rather simple, but are new compounds barely accessible by conventional methods.

Scheme 3



Scheme 4



Functionalized silyl anions in solution are observable by ^{13}C, ^{29}Si and ^{7}Li NMR spectroscopies. In the ^{13}C NMR spectra,[4i,j] aromatic carbons in **1** in THF

appear at 158.5 (ipso), 135.6 (ortho), 126.6 (meta), and 123.9 (para) ppm and chemical shift changes from the corresponding chlorosilane precursors $\Delta\delta$(SiLi - SiCl) are +24.3 (ipso), 0 (ortho), -2.1 (meta), and -7.3 (para) ppm (positive signs denote downfield shifts) (Table 1 and Figure 1). The pattern of charge distribution is consistent with that of π-polarization, which shows sharp contrast to the pattern of charge distribution of carbanion (resonance effect).[4j] The data are quite similar to those for $MePh_2SiLi$[4j] and may imply that the Et_2N group exhibits an effect similar to the Me group on the charge distribution in the anions.

The ^{29}Si NMR spectra of **1**, **2**, and **3**, however, are quite different from those of ordinary (triorganosilyl)lithiums (Table 2).[4i,k,l] The chemical shift of **1** was observed at 19.3 ppm. This is a large downfield shift compared to the corresponding chlorosilane **8** (-6.3 pm)($\Delta\delta$ = +26.1) and exhibits a remarkable contrast to the upfield shift of (triorganosilyl)lithiums compared to chlorosilanes, for example $\delta(Ph_2MeSiLi)$ = -20.5 and $\delta(Ph_2MeSiCl)$ = 10.0 ($\Delta\delta$ = -30.5).[4i,16] Replacing of the Me group with the Et_2N group on the (aminosilyl)lithium induces the larger downfield shift ($\Delta\delta$ = +13.5) than with phenyl group ($\Delta\delta$ = +4.9). The data suggest that the electronegative Et_2N group contributes significantly to the electronic structure of the (aminosilyl)lithiums (Table 2).

The $^{29}Si-^{7}Li$ and $^{29}Si-^{6}Li$ scalar couplings of the (aminosilyl)lithiums are successfully observed in THF or less polar solvent, 2-methyl-THF (MTHF) at low temperatures (Table 2 and Figure 2). The ^{29}Si resonance of ^{7}Li (I = 3/2) derivatives of **1** - **3** resolves into a quartet, respectively: especially, $(Et_2N)_2PhSi^{7}Li$ (**2**), shows a well resolved quartet ($J[^{29}Si-^{7}Li]$ = 56.5 Hz) even at 173 K. This implies that ^{29}Si is coupled with one ^{7}Li atom. The ^{29}Si resonance of ^{6}Li (I = 1) derivatives of **1** - **3** resolves into a triplet, respectively. This implies again that ^{29}Si is coupled with one ^{6}Li atom. All the data suggest that **1** - **3** exist as monomeric structures in THF and MTHF solution. It is noted that the exchange rate of Li is decreased and the coupling constant is increased with an increase in the number of the Et_2N group.

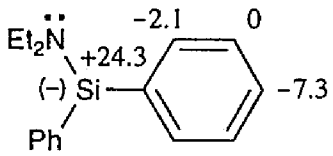
The ^{7}Li NMR spectra of **1**, **2**, and **3** are similar to those of (triorganosilyl)lithiums as shown in Table 2. The downfield shifts relative to LiCl

may suggest that the (aminosilyl)lithiums exist as contact ion pairs in THF solution.[4l]

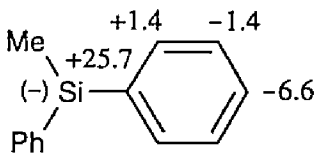
Table 1. ^{13}C Chemical Shifts of (Aminosilyl)lithiums[a]

	ipso	ortho	meta	para
$(Et_2N)Ph_2SiLi$ (**1**)	158.5	135.6	126.6	123.9
$(Et_2N)_2PhSiLi$ (**2**)	160.0	134.9	126.6	123.2
$(Et_2N)PhMeSiLi$ (**3**)	164.8	133.7	126.5	122.7
$(Et_2N)Ph_2SiCl$ (**8**)	134.3	135.6	128.7	131.2
$(Et_2N)_2PhSiCl$ (**9**)	(135.5)	135.5	128.5	130.8
$(Et_2N)PhMeSiCl$ (**10**)	135.7	134.8	128.6	130.9
$Ph_2MeSiLi$ [b]	160.1	135.4	126.7	123.9
$Ph_2MeSiCl$ [b]	134.4	134.0	128.1	130.5

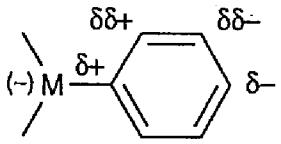
[a] The spectra were recorded in THF (0.3 M) as solvent with external THF-d_8 for D-lock and cyclohexane as reference (δ 27.7).
[b] Reference 4j.



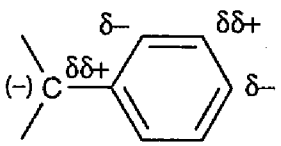
Δδ (SiLi-SiCl)



Δδ (SiLi-SiCl) reference 4j



π-Polarization



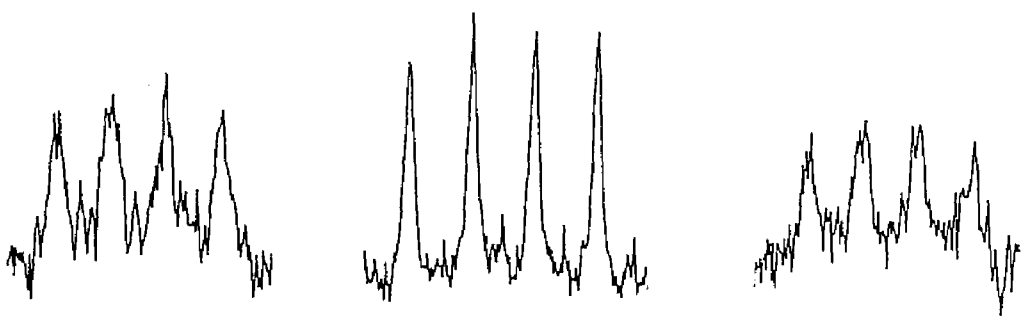
Resonance

Figure 1. ^{13}C chemical shift changes from chlorosilanes to the corresponding silyllithiums.

Table 2. ^{29}Si NMR and ^{7}Li NMR Chemical Shifts and $^{29}Si-^{7}Li$ and $^{29}Si-^{6}Li$ Couplings of (Aminosilyl)lithiums.[a]

	^{29}Si shifts and couplings			^{7}Li shifts
	δ (273 K)[b]	$^{1}J[^{29}Si-^{7}Li]$, Hz[c]	$^{1}J[^{29}Si-^{6}Li]$, Hz[c]	δ (273 K)
$(Et_2N)Ph_2SiLi$ (**1**)	19.3	q, 48 (163 K)	t, 18 (173 K) (MTHF)	0.49
$(Et_2N)_2PhSiLi$ (**2**)	27.9	q, 57 (173 K) (1.0M)	t, 22 (173 K)	0.35
$(Et_2N)PhMeSiLi$ (**3**)	14.4	q, 51 (163 K)	t, 20 (163 K)	0.37
$(Et_2N)Ph_2SiCl$ (**8**)	-6.8			
$(Et_2N)_2PhSiCl$ (**9**)	-18.8			
$(Et_2N)PhMeSiCl$ (**10**)	2.3			
$Ph_2MeSiLi$ [e]	-20.5		t, 15 (158 K)	0.61
$Ph_2MeSiCl$ [e]	10.0			

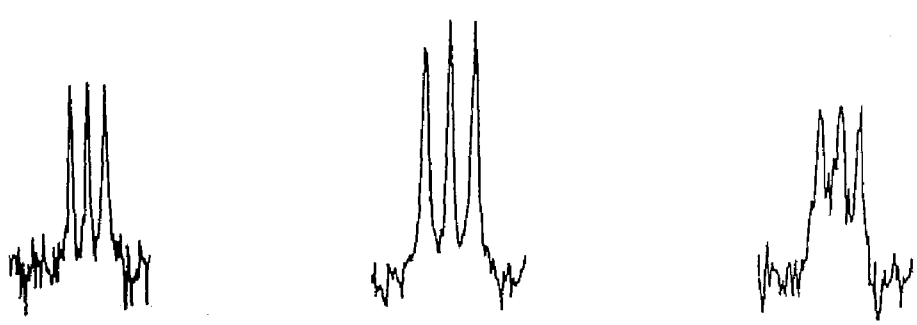
[a] The spectra were recorded in an unlocked mode.
[b] A 1.0 M THF solution with external tetramethylsilane as reference (0.0 ppm).
[c] A 0.3 M THF solution, otherwise noted, with internal tetramethylsilane as reference (0.0 ppm).
[d] A 0.3 M THF solution with external 0.3 M LiCl/MeOH as reference (0.0 ppm).
[e] References 4i, 4k, and 4l.



$(Et_2N)Ph_2Si$-^7Li (**1**)
163K, THF

$(Et_2N)_2PhSi$-^7Li (**2**)
173K, THF

$(Et_2N)PhMeSi$-^7Li (**3**)
163K, THF



$(Et_2N)Ph_2Si$-^6Li (**1**)
173K, MTHF

$(Et_2N)_2PhSi$-^6Li (**2**)
173K, THF

$(Et_2N)PhMeSi$-^6Li (**3**)
163K, THF

Figure 2. Low-temperature ^{29}Si NMR spectra of (aminosilyl)lithiums.

Experimental Section

General Remarks. ^{1}H (200 MHz) NMR and ^{13}C (50.29 MHz) NMR spectra were recorded on a Varian VXR-200 spectrometer. ^{29}Si (53.67 MHz) NMR and ^{7}Li (105.014MHz) spectra were recorded on a JEOL EX-270 spectrometer. ^{1}H and ^{13}C chemical shifts are referenced to internal benzene-d_6 (^{1}H δ 7.200 ppm and ^{13}C δ 128.00 ppm) or $CDCl_3$ (^{13}C δ 77.00 ppm), otherwise stated. Mass spectra were measured on a JEOL JMS-D300 mass spectrometer connected with a JEOL LGC-20K gas chromatograph, equipped with a 1-m glass column packed with OV-17 (3%) on Chromosorb. The elemental analyses were performed at the Microanalysis Center of Kyoto University: Analytical samples were purified by preparative GLC or preparative MPLC. GLC analysis was performed on a Shimadzu GC-4B gas chromatographed, equipped with 3-m or 1-m column packed with 30% Silicone DC550 on Celite 545. Column chromatography was performed by using Kieselgel 60 (70-230 mesh) (Merck). Thin layer chromatography (TLC) was performed on plates of silica gel 60F-254 (Merck). Preparative medium pressure liquid chromatography (MPLC) was performed with a silica gel prepacked C.I.G. (Si-10) column (Kusano).

(Diethylamino)diphenylchlorosilane (**8**), bis(diethylamino)phenylchlorosilane (**9**), and (diethylamino)phenylmethylchlorosilane (**10**) were prepared according to the procedure of the literature.[15] Trimethylcholorostannane was prepared by disproportionation between tetramethylstannane and dimethyldichlorostannane:[17] the last was kindly donated from the Nitto Kasei Co. Lithium dispersion (25 wt. % in mineral oil) was purchased from Aldrich. Lithium granular was purchased from Chemetall Gesellshaft. Lithium-6 metal (95 atom% ^{6}Li) was purchased from Aldrich. *n*-Butyllithium in hexane was purchased from Wako Pure Chemical Industries. *tert*-Butyllithium in pentane was purchased from Kanto Chemicals. 12-Crown-4 was purchased from Aldrich. Ether, THF, and 2-methyl-THF (MTHF) were distilled under nitrogen from sodium/benzophenone. Hexane was dried over sodium wire and distilled under nitrogen. Diethylamine, triethylamine, and isopropyl alcohol were distilled from calcium hydride. Tetramethylethylenediamine

(TMEDA) was distilled from *n*-butyllithium. Acetyl Chloride was distilled from phosphorous pentachloride. All reactions were carried out under a nitrogen or an argon atmosphere.

NMR Measurement of the Silyllithiums 1 - 3 and the Precursors Chlorosilanes. The NMR samples of **1 - 3** were prepared from the corresponding (amino)chlorosilanes **8 - 10** and lithium metal in THF or MTHF. ^{13}C chemical shifts were referenced to internal cyclohexane (27.7 ppm). The solution (0.5 M, 0.3 mL) was transferred by means of a syringe into an NMR sample tube and THF-d_8 (0.2 mL) was added for D-lock under a nitrogen atmosphere. ^{29}Si chemical shifts were referenced to external (at 273 K) or internal (at 173 K and 163 K) tetramethylsilane (0 ppm). The ^{29}Si NMR spectra were observed in an unlocked mode. Although the spectrometer was unlocked during the acquisition, the field was stable and no significant field shift was observed. For the NMR measurements, the solution (0.3 or 1.0 M) was transferred to an NMR sample tube via a Teflon tube under an argon atmosphere. ^{7}Li chemical shifts were referenced to external 0.3 M LiCl/MeOH (0.0 ppm). The ^{7}Li NMR spectra were observed in an unlocked mode. For the NMR measurements, the solution (0.3 M) was transferred to an NMR sample tube via a Teflon tube under an argon atmosphere.

(Diethylamino)diphenylchlorosilane (8). ^{1}H NMR (C_6D_6): δ 0.96 (t, J = 7.1 Hz, 6H), 2.90 (q, J = 7.1 Hz, 4H), 7.17-7.23 (m, 6H), 7.89-7.94 (m, 4H). ^{13}C NMR (C_6D_6): δ 10.67, 35.68, 124.32, 126.67, 130.01, 131.30.

Bis(diethylamino)phenylchlorosilane (9). ^{1}H NMR (C_6D_6): δ 1.00 (t, J = 7.0 Hz, 12H), 2.95 (q, J = 7.0 Hz, 4H), 2.96 (q, J = 7.0 Hz, 4H), 7.23-7.28 (m, 3H), 7.88-7.93 (m, 2H). ^{13}C NMR (C_6D_6): δ 14.63, 39.00, 128.13, 130.37, 135.17 (2C).

(Diethylamino)phenylmethylchlorosilane (10). ^{1}H NMR (C_6D_6): δ 0.55 (s, 3H), 0.93 (t, J = 7.0 Hz, 6H), 2.79 (q, J = 7.0 Hz, 2H), 2.80 (q, J = 7.0

Hz, 2H), 7.23-7.26 (m, 3H), 7.80-7.85 (m, 2H). ^{13}C NMR (C_6D_6): δ 1.50, 15.06, 39.90, 128.23, 130.48, 134.51, 135.31.

A Typical Procedure for the Synthesis of (Aminosilyl)stannanes: Preparation of [(Diethylamino)diphenylsilyl]trimethylstannane (4). A solution of trimethylchlrorostannane (22.5 g, 111 mmol) in THF (25 mL) was added dropwise to a suspension of lithium granular (3.30 g 475mg-atom) in THF (40 mL) over 20 min at 0 °C and stirred for 5 h at room temperature to a greenish solution.[18] After removing unreacted lithium metal, the greenish solution was added to a solution of (diethylamino)diphenylchlorosilane (**8**) (24.8 g, 85.4 mmol) in THF (100 mL) at room temperature and the reaction mixture was stirred overnight. The volatile materials were evaporated under reduced pressure. The residue was diluted with hexane, filtered, and the filtrate was concentrated. The residue was distilled (147-150 °C/0.40 mmHg) to give **4** (31.1 g, 87% yield) as colorless oil. ^1H NMR (C_6D_6): δ 0.33 (s, 9H), 0.99 (t, J = 7.0 Hz, 6H), 2.99 (q, J = 7.0 Hz, 4H), 7.24-7.30 (m, 6H), 7.68-7.72 (m, 4H). ^{13}C NMR (C_6D_6): δ -10.07, 15.60, 42.18, 128.32, 129.50, 135.24, 138.68. MS: *m/e* 403 (M^+-Me). Anal. Calcd for $C_{19}H_{29}NSiSn$: C, 54.56; H, 6.99. Found: C, 54.67; H, 7.12.

[Bis(diethylamino)phenylsilyl]trimethylstannane (5). bp 140-150 °C/0.9 mmHg (bath temperature). ^1H NMR (C_6D_6): δ 0.36 (s, 9H), 1.03 (t, J = 7.0 Hz, 12H), 2.98 (q, J = 7.0 Hz, 8H), 7.28-7.31 (m, 3H), 7.70-7.75 (m, 2H). ^{13}C NMR (C_6D_6): δ -9.61, 15.28, 40.28, 128.23, 129.35, 134.52, 140.31. MS: *m/e* 414 (M^+). Anal. Calcd for $C_{17}H_{34}N_2SiSn$: C, 49.41; H, 8.29. Found: C, 49.41; H, 8.29.

Reaction of 4 with *n*-Butyllithium: Synthesis of [(Diethylamino)diphenylsilyl]lithium (1) and Trapping as 1-Diethylamino-1,1-diphenyl-2,2,2-trimethyldisilane (6) in THF. To a solution of **4** (990 mg, 2.37 mmol) in THF (10.0 mL) was added *n*-butyllithium in hexane (1.42 mL, 2.37 mmol) at 0 °C. The mixture was stirred at 0 °C for 20 min to

give a solution of **1**. To the mixture was added trimethylchlorosilane (0.300 mL, 2.37 mmol). After being stirred for further 30 min at 0 °C, the mixture was warmed to the amibient temperature. The volatile materials were evaporated under reduced pressure. The residue was diluted with hexane (10 mL), filtered, and concentrated. The residue was subjected to bulb-to-bulb distillation (155–165 °C/1.50 mmHg, bath temperature) to give **6** (671 mg, 86% yield) as colorless oil. ^{1}H NMR (C_6D_6): δ 0.25 (s, 9H), 1.00 (t, J = 7.0 Hz, 6H), 3.03 (q, J = 7.0 Hz, 4H), 7.26–7.30 (m, 6H), 7.71–7.75 (m, 4H). ^{13}C NMR (C_6D_6): δ -0.73, 15.44, 41.82, 128.13, 129.19, 135.49, 138.46. MS: *m/e* 327 (M^+). Anal. Calcd for $C_{19}H_{29}NSi_2$: C, 69.66; H, 8.92. Found: C, 69.72; H, 9.16.

Reaction of 4 with *n*-Butyllithium: Synthesis of [(Diethylamino)diphenylsilyl]lithium (1) and Trapping as 1-Diethylamino-1,1-diphenyl-2,2,2-trimethyldisilane (6) in THF-Et_2O. To a solution of **4** (451 mg, 1.08 mmol) in THF (4.0 mL) and Et_2O (1.0 mL) was added *n*-butyllithium in hexane (0.690 mL, 1.19 mmol) at 0 °C. The mixture was stirred at 0 °C for 20 min to give a solution of **1**. To the solution was added trimethylchlorosilane (0.151 mL, 1.19 mmol). After being stirred for 3 min at 0 °C, the mixture was warmed to the ambient temperature. The yield of **6** was estimated by means of GLC analysis (90%): Docosane was used as internal standard.

Reaction of 5 with *tert*-Butyllithium: Synthesis of [Bis(diethylamino)phenylsilyl]lithium (2) and Trapping as 1,1-Bis(diethylamino)-1-diphenyl-2,2,2-trimethyldisilane (7). To a solution of **5** (513 mg, 1.15 mmol) and TMEDA (0.520 mL, 3.45 mmol) in THF (4.0 mL) was added *tert*-butyllithium in pentane (2.33 mL, 3.45 mmol) at -78 °C. The reaction mixture was warmed to -30 °C over 1 h, and stirred for 3 h at that temperature to give a solution of **2**. To the solution was added trimethylchlorosilane (0.437 mL, 3.45 mmol) at -30 °C. The mixture was warmed to the ambient temperature. The yield of **7** was estimated by means of GLC analysis (77%): Docosane was used as internal standard. The pure sample was obtained as colorless

oil by preparative GLC. bp 150-170 °C/1.8 mmHg (bath temperature). ^{1}H NMR (C_6D_6): δ 0.26 (s, 9H), 1.07 (t, J = 6.9 Hz, 12H), 3.02 (q, J = 6.9 Hz, 8H), 7.29-7.34 (m, 2H), 7.74-7.78 (m, 3H). ^{13}C NMR (C_6D_6): δ 0.23, 15.73, 40.23, 128.00, 129.02, 135.22, 139.76. MS: m/e 327 (M^+). Anal. Calcd for $C_{17}H_{34}N_2Si_2$: C, 63.29; H, 10.62. Found: C, 63.13; H, 10.57.

Typical Procedure for Reaction of (Amino)chlorosilane with Lithium: Synthesis of [(Diethylamino)diphenylsilyl]lithium (1). To a suspension of lithium dispersion (16 mg-atom, commercial 25 wt % in mineral oil was washed with dry hexane three times) in THF (8.0 mL) was added dropwise (amino)chlorosilane **8** (830 mg, 4.00 mmol) at room temperature. After a few minutes of stirring, the resulting greenish mixture was stirred at 0 °C for 4 h to give a solution of **1** in 98% yield. The yield of **1** was estimated by means of GLC analysis of **6** obtained by trapping with trimethylchlorosilane: Docosane was used as internal standard. Lithium granular can also be used for preparation of **1**.

[Bis(diethylamino)phenylsilyl]lithium (2). (Diaminosilyl)lithium **2** was prepared from **7** by the same method as described above in 97% yield. The yield of **2** was estimated by means of GLC analysis of **7** obtained by trapping with trimethylchlorosilane: Docosane was used as internal standard.

[(Diethylamino)phenylmethylsilyl]lithium (3) and Trapping as 1-Diethylamino-1-phenyl-1,2,2,2-tetramethyldisilane (11). To a suspension of lithium dispersion (18 mg-atom, commercial 25 wt % in mineral oil was washed with dry hexane three times) in THF (10.0 mL) was added dropwise (amino)chlorosilane **8** (1.01 g, 4.43 mmol) at room temperature. After a few minutes of stirring, the resulting greenish mixture was stirred at 0 °C for 24 h to give a solution of **3** in 80% yield. The yield of **3** was estimated by means of GLC analysis of **11** obtained by quenching with trimethylchlorosilane: Eicosane was used as internal standard. The pure sample was obtained as colorless oil by preparative GLC. bp 110-130 °C/1.8 mmHg. ^{1}H NMR (C_6D_6): δ 0.19 (s, 9H), 0.49 (s, 3H),

1.01 (t, J = 7.0 Hz, 6H), 2.92 (q, J = 7.0 Hz, 4H), 7.26-7.31 (m, 2H), 7.62-7.67 (m, 2H). ^{13}C NMR (C_6D_6): δ -2.07, -1.41, 15.86, 41.69, 128.20, 128.90, 134.36, 140.67. MS: m/e 265 (M^+). Anal. Calcd for $C_{14}H_{27}NSi_2$: C, 63.32; H, 10.25. Found: C, 63.18; H, 10.41.

Typical Procedure for Coupling of (Aminosilyl)lithium with Chlorosilane: Synthesis of 1-Diethylamino-1,1-diphenyl-2-vinyl-2,2-dimethyldisilane (15). To a solution of **1** (2.4 mmol) in THF (5.0 mL), which was prepared from **8** and lithium dispersion, was added (vinyl)(dimethyl)chlorosilane via a syringe at 0 °C. The reaction mixture was stirred for 1 h at 0 °C and warmed to the ambient temperature. The volatile materials were removed under reduced pressure. The residue was diluted with hexane (15 mL), filtered, and the filtrate was concentrated. The residue was subjected to bulb-to-bulb distillation (170-190 °C/1.5 mmHg, bath temperature) to give **15** (500 mg, 60%) as colorless oil. ^1H NMR (C_6D_6): δ 0.32 (s, 6H), 1.01 (t, J = 7.0 Hz, 6H), 3.04 (q, J = 7.0 Hz, 4H), 5.71 (dd, J = 3.7 and 20.0 Hz), 5.96 (dd, J = 3.7 and 14.5 Hz), 6.38 (dd, J = 14.5 and 20.0), 7.26-7.30 (m, 6H), 7.73-7.77 (m, 4H). ^{13}C NMR ($CDCl_3$): δ -3.09, 15.19, 41.33, 127.62, 128.77, 131.63, 135.20, 137.95, 139.05. MS: *m/e* 339 (M^+). Anal. Calcd for $C_{20}H_{29}NSi_2$: C, 70.03; H, 8.61. Found: C, 69.69; H, 8.75.

1-Diethylamino-1,1-diphenyl-2,2-dimethyldisilane (12). bp 145-165 °C/1.10 mmHg (bath temperature). ^1H NMR (C_6D_6): δ 0.26 (d, J = 4.5 Hz, 6H), 1.00 (t, J = 7.0 Hz, 6H), 3.02 (q, J = 7.0 Hz, 4H), 4.35 (septet, J = 4.5 Hz, 1H), 7.26-7.31 (m, 6H), 7.71-7.76 (m, 4H). ^{13}C NMR (C_6D_6): δ -5.65, 15.53, 41.82, 128.22, 129.38, 135.49, 137.96. MS: *m/e* 313 (M^+). Anal. Calcd for $C_{18}H_{27}NSi_2$: C, 68.94; H, 8.68. Found: C, 68.93; H, 8.77.

1,2-Bis(diethylamino)-1,1-diphenyl-2,2-dimethyldisilane (13). bp 190-220 °C/1.3 mmHg (bath temperature). ^1H NMR (C_6D_6): δ 0.41 (s, 6H), 0.88 (t, J = 7.0 Hz, 6H), 1.05 (t, J = 7.0 Hz, 6H), 2.80 (q, J = 7.0 Hz, 4H), 3.12

(q, J = 7.0 Hz, 4H), 7.28-7.31 (m, 6H), 7.80-7.84 (m, 4H). ^{13}C NMR (C_6D_6): δ 1.17, 15.17, 15.69, 41.16, 41.57, 128.00, 129.04, 135.67, 139.21. MS: *m/e* 384 (M^+). Anal. Calcd for $C_{22}H_{36}N_2Si_2$: C, 68.69; H, 9.43. Found: C, 68.45; H, 9.40.

1-Isopropoxy-2-diethylamino-2,2-diphenyl-1,1-dimethyldisilane (14). bp 167-187 °C/1.5 mmHg (bath temperature).^1H NMR (C_6D_6): δ 0.40 (s, 6H), 1.02-1.10 (m, 12H), 3.12 (q, J = 7.0 Hz, 4H), 3.86 (septet, J = 6.0 Hz, 1H), 7.28-7.31 (m, 6H), 7.82-7.86 (m, 4H). ^{13}C NMR (C_6D_6): δ 1.25, 15.39, 25.97, 41.69, 65.90, 128.11, 129.24, 135.71, 138.37. MS: *m/e* 371 (M^+). Anal. Calcd for $C_{21}H_{33}NOSi_2$: C, 67.86; H, 8.95. Found: C, 67.51; H, 9.05.

Typical Procedure for Conversion of (Diethylamino)disilane into (Chloro)disilane: Synthesis of 1-Chloro-1,1-diphenyl-2,2-dimethyldisilane (16). To **12** (158 mg, purity >90%, 0.45 mmol) was added acetylchloride (0.36 mL, 0.50 mmol) at 0 °C. The mixture was stirred for 1 h and warmed to the ambient temperature. The mixture was subjected to bulb-to-bulb distillation (120-150 °C/1.2 mmHg, bath temperature) to give **16** (124 mg, purity 84%) in 84% yield. ^1H NMR (C_6D_6): δ 0.22 (d, J = 4.4 Hz, 6H), 4.32 (septet, J = 4.4 Hz, 1H), 7.14-7.17 (m, 6H), 7.70-7.77 (m, 4H). ^{13}C NMR (C_6D_6): δ 2.92, 128.61, 129.98, 134.77, 136.12. MS: *m/e* 278 (M^++2), 276 (M^+). Anal. Calcd for $C_{14}H_{17}Si_2Cl$: C, 60.72; H, 6.19. Found: C, 60.74; H, 6.30.

1,2-Dichloro-1,1-diphenyl-2,2-dimethyldisilane (17). bp 180-200 °C/1.30 mmHg (bath temperature). ^1H NMR (C_6D_6): δ 0.47 (s, 6H), 7.14-7.17 (m, 6H), 7.77-7.82 (m, 4H). ^{13}C NMR (C_6D_6): δ 1.68, 128.68, 130.98, 134.90, 136.97.

1,3-Bis(isopropoxy)-1,1,3,3-tetraphenyl-2,2-dimethyltrisilane (18). To a solution of **1** (4.22 mmol) in THF (5.0 mL) was added 12-crown-4 (0.700 mL, 4.30 mmol) at 0 °C and the solution was stirred for 10 min. To the

solution was added dimethyldichlorosilane (0.170 mL, 1.41 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 18 h and warmed to the ambient temperature. The volatile materials were removed under reduced pressure. The residue was diluted with benzene (20 mL), filtered, and the filtrate was concentrated. Removing the impurities by bulb-to-bulb distillation (up to 200 °C/1.0 mmHg) to give crude 1,3-bis(diethylamino)-1,1,3,3-tetraphenyl-2,2-dimethyltrisilane (958 mg) as residue. To the residue was added NH_4Cl (40 mg, 0.70 mmol) and isopropyl alcohol (5.0 mL) at room temperature. After being stirred for 24 h, the volatile materials were removed under reduced pressure. The residue was diluted with hexane (20 mL), filtered, and the filtrate was concentrated. The residue was subjected to column chromatography on silica gel (50 mL) eluted with hexane/AcOEt (40/1) to afford **18** (423 mg, overall 56% yield based on dimethyldichlorosilane) (R_f = 0.28) as colorless oil. ^1H NMR (C_6D_6): δ 0.45 (s, 6H), 1.13 (d, J = 6.1 Hz, 12H), 4.11 (septet, J = 6.1 Hz, 2H), 7.23–7.26 (m, 8H), 7.75–7.80 (m, 12H). ^{13}C NMR ($CDCl_3$): δ −5.05, 25.77, 66.87, 127.62, 129.25, 135.15, 136.84. MS: *m/e* 540 (M^+). Anal. Calcd for $C_{32}H_{40}O_2Si_3$: C, 71.05; H, 7.45. Found: C, 71.03; H, 7.56.

1-Chloro-1,1-diphenyl-2,2,2-trimethyldisilane (19). bp 119–121 °C/0.70 mmHg. ^1H NMR (C_6D_6): δ 0.23 (s, 9H), 7.17–7.20 (m, 4H), 7.71–7.75 (m, 6H). ^{13}C NMR ($CDCl_3$): δ −2.24, 128.14, 130.06, 134.34, 134.72.

Synthesis 1-Diethylamino-1,2,2-triphenyl-1,3,3,3-tetramethyltrisilane (20). To a solution of **3**, which was prepared from **10** (462 mg, 1.93 mmol) and lithium dispersion (11.2 mg-atom), and TMEDA (0.320 mL, 2.12 mmol) in THF (4.0 mL) was added a solution of **19** (609 mg, 2.01 mmol) in THF (3.0 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 7 h and warmed to the ambient temperature. The volatile materials were removed under reduced pressure. The residue was diluted with hexane (30 mL), filtered, and the filtrate was concentrated. The residue was subjected to bulb-to-bulb distillation (up to 300 °C/1.5 mmHg) to give the crude **20** (546 mg) as colorless oil. Removing the

impurities by bulb-to-bulb distillation (up to 170 °C/1.2 mmHg) to give pure **20** as colorless residue. ^{1}H NMR (C_6D_6): δ 0.20 (s, 9H), 0.71 (s, 3H), 0.90 (t, J = 7.0 Hz, 6H), 2.95 (q, J = 7.0 Hz, 4H), 7.20-7.25 (m, 9H), 7.63-7.78 (m, 6H). ^{13}C NMR (C_6D_6): δ -0.73, 1.82, 127.82, 128.00, 128.48, 129.36, 133.33, 134.68, 136.12, 139.66. MS: m/e 447 (M^+). Anal. Calcd for $C_{26}H_{37}NSi_3$: C, 69.73; H, 8.33. Found: C, 69.90; H, 8.37.

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Chapter 2

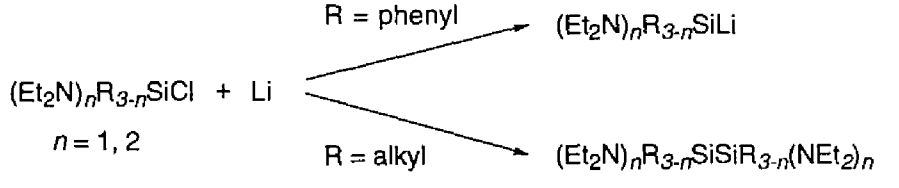
Coupling of (Amino)alkylchlorosilanes with Lithium: A New Access to Symmetrical Di- and Tetrafunctionalized Alkyldisilanes

Abstract: Homocoupling reactions of amino- and diaminoalkylchlorosilanes with lithium metal proceed readily in THF at room temperature to form the corresponding symmetrical diamino- and tetraaminoalkyldisilanes, respectively, in high yields, which are transformed into chloro- and alkoxyalkyldisilanes under mild conditions.

Introduction

In chapter 1, the author described the synthesis of (amino)phenylsilyl anions as the first stable functionalized silyl anions by the reaction of (amino)*phenyl*silyl chlorides with lithium.[1] The author now finds that the action of lithium on (amino)*alkyl*silyl chlorides results in the formation of not the silyl anions but the corresponding coupling products, symmetrical polyfunctionalized disilanes, as shown in Scheme 1.

Scheme 1



There have been only two methodologies for the synthesis of polyfunctionalized alkyldisilanes:[2] (1) functional group transformation of the "disilane fraction" $Si_2Me_{6-n}Cl_n$ (n = 3,4) in the industrial direct synthesis of methylchlorosilanes[3] and (2) demethylation of hexamethyldisilane or dephenylation of phenylalkyldisilanes by the action of strong electrophilic agents such as sulfuric

acid (followed by treatment with ammonium halide),[3,4] trifluoromethanesulfonic acid,[5] $HCl/AlCl_3$,[6-8] and $MeCOCl/AlCl_3$.[7] The present coupling reaction provides the third method, which should be more convenient and versatile for the synthesis of symmetrical functionalized disilanes containing a variety of alkyl groups in view of the ready availability of (amino)alkylsilyl chlorides[9] and facile functional group transformations under mild conditions.

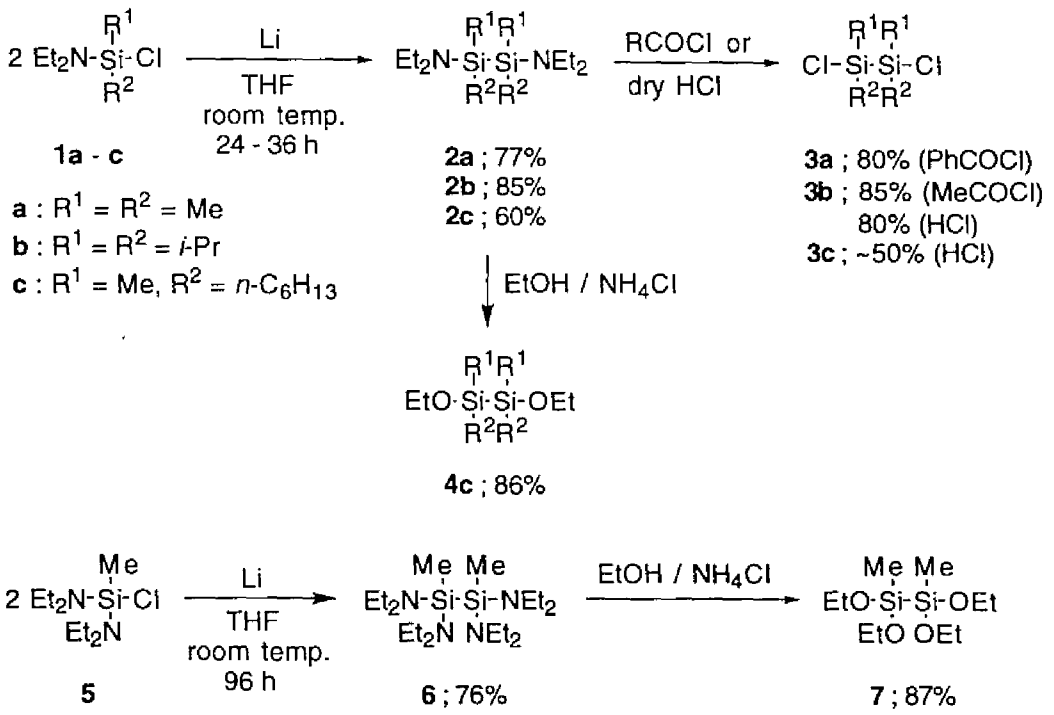
Results and Discussion

Several representative results are summarized in Scheme 2. Aminochlorosilanes **1** and **5** are readily prepared by treatment of the corresponding dichloro- and trichlorosilanes with 1 equiv and 2 equiv of diethylamine, respectively, in the presence of a slightly excess amount of triethylamine in ether, followed by filtration and distillation.[3] The coupling reaction of **1** with lithium dispersion in THF proceeded smoothly at room temperature in 1 - 1.5 day under an nitrogen atmosphere to afford diaminodisilanes **2**. Alkyl groups on silicon may be not only methyl (**2a**) but also sterically crowded isopropyl (**2b**) and long alkyl chains such as *n*-hexyl group (**2c**). In the last case an almost 1:1 mixture of *meso* and *dl* stereoisomers was formed. Diaminochlorosilane **5** was considerably less reactive than **1** and required a longer period of time to give tetraaminodimethyldisilane **6** in moderate yields. These reaction conditions are similar to that for the coupling of trimethylchlorosilane with lithium.[10] **Caution** in the isolation step: Filtration of the excess lithium metal in the air may cause ignition of the lithium-containing filter cake. The following two-step filtration is recommended: The remaining lithium dispersion is filtered briefly first through glass wool under nitrogen and the filtrate that contains the salt is then filtered safely in the air. The clear filtrate is concentrated and distilled under reduced pressure to give pure **2** and **6**.

Although the coupling reactions proceeded faster under reflux conditions in THF, satisfactory results were obtained in only one case. Thus, the reaction of **1a** with lithium under THF reflux was completed in 6 h, much faster than 1 day at room temperature, to give **2a** of high purity in the comparable yield (74%). In other

cases, however, the coupling products were obtained only in much lower yields and in lower purities. Reactions were also considerably accelerated by ultrasonication,[11] but the yields and purities were decreased greatly. These refluxing and sonication are thus *not* recommended for the present disilane synthesis.

Scheme 2

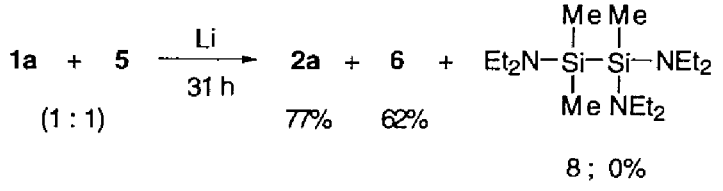


The resulting aminodisilanes are converted into the corresponding chlorodisilanes or alkoxydisilanes,[12] as shown in Scheme 2. Thus, **2a** and **2b** were treated with two equiv of benzoyl chloride and with excess amount of acetyl chloride, respectively, to afford the corresponding dichlorodisilane **3a** and **3b**. The latter was also obtained by the action of dry hydrogen chloride[13] on **2b** in THF. The author has encountered, however, some problems in transformations of **2c** and **6** under similar conditions. Thus, while with hydrogen chloride **2c** afforded dichlorodisilane **3c** in about 50% yield together with uncharacterizable non-volatile by-products, only a complex mixture of product was formed from **2c** and **6** with acetyl chloride; the reason remained to be clarified. Ethanolysis of these

aminodisilanes, however, proceeded readily to form the corresponding ethoxydisilanes cleanly. Thus **2c** and **6** afforded **4c** and **7**, respectively, in high yields.

In order to get unsymmetrical functionalized disilanes and oligosilanes by cross-coupling of two different chlorosilanes, the author has attempted a variety of combinations without success so far. For example, as shown in Scheme 3, a 1 : 1 mixture of **1a** and **5** afforded a mixture of homocoupling products **2a** and **6** in high yields, without formation of the cross-coupling product, triaminodisilane **8**.[14] The author has obtained no appreciable amounts of cross-coupling products in other combinations such as **1a** / Me_3SiCl, **1a** / $MeSiCl_3$, and **5** / Me_3SiCl, suggesting rather unusual behavior of aminochlorosilanes toward lithium-coupling.

Scheme 3



Experimental Section

General Remarks. ^1H NMR (200 MHz) spectra were recorded on a Varian VXR-200 spectrometer. The elemental analyses were performed at the Microanalysis Center of Kyoto University: Analytical samples were purified by preparative GLC. GLC analysis was performed on a Shimadzu GC-4B gas chromatographed, equipped with 3-m or 1-m column packed with 30% Silicone DC550 on Celite 545. Ether and THF were distilled under nitrogen from sodium/benzophenone. Hexane was dried over sodium wire and distilled under nitrogen. Diethylamine and triethylamine were distilled from calcium hydride. Diisopropyldichlorosilane was commercially available. Lithium dispersion (25 wt.

% in mineral oil) was purchased from Aldrich. All reactions were carried out under a nitrogen atmosphere.

Preparation of Aminnochlorosilanes 1 and 4. Known compounds **1a**[9,15] and **4**[16] were prepared in essentially the same method as described below.

Diisopropyl(diethylamino)chlorosilane (1b). To a mixture of diisopropyldichlorosilane (12.6 mL, 70 mmol), triethylamine (10.8 mL, 77 mmol), and dry THF (70 mL) was added slowly a solution of diethylamine (7.4 mL, 70 mmol) in THF (10 mL) at 0 °C over 30 min. The white mixture was allowed to warm to room temperature, stirred for 24 h, diluted with hexane, and filtered with suction. The filtrate was evaporated and the residue was distilled under reduced pressure to give 11.0 g (71% yield) of **1b**: bp 51–53 °C/0.9 mmHg. ^{1}H NMR (C_6D_6): δ 0.97 (t, J = 7.0 Hz, 6H), 1.05–1.20 (m, 14H), 2.81 (q, J = 7.0 Hz, 4H). Anal. Calcd for $C_{10}H_{24}NSiCl$: C, 54.14; H, 10.90. Found: C, 53.98; H, 10.91.

***n*-Hexylmethyl(diethylamino)chlorosilane (1c).** This compound was obtained in 72% yield in a similar manner from *n*-hexylmethyldichlorosilane, readily available by platinum-catalyzed hydrosilation of 1-hexene with methyldichlorosilane: bp 74–75 °C/1.0 mmHg. ^{1}H NMR (C_6D_6): δ 0.40 (s, 3H), 0.85–1.02 (m, 5H), 0.98 (t, J = 7.0 Hz, 6H), 1.20–1.65 (m, 8H), 2.80 (q, J = 7.0 Hz, 4H). Anal. Calcd for $C_{11}H_{26}NSiCl$: C, 56.01; H, 11.11. Found: C, 55.79; H, 11.38.

Preparation of Aminodisilanes 2 and 6. 1,2-Bis(diethylamino)-1,1,2,2-tetramethyldisilane (2a). A solution of **1a** (1.57 g, 9.46 mmol) in dry THF (3 mL) was added to a suspension of lithium dispersion (41.8 mg-atom) in THF (5 mL) at room temperature under an inert atmosphere. The mixture was stirred for 24 h at room temperature. The complete disappearance of **1a** was confirmed by GLC analysis. The mixture was then filtered through a short pad of glass wool under a nitrogen atmosphere. After concentration of the filtrate under

reduced pressure, the residue was diluted with dry hexane and filtered through a glass fiber pad safely in the air. The filtrate was concentrated and the residue was purified by bulb-to-bulb distillation under reduced pressure to give 1.07 g (77% yield) of **2a** as a colorless liquid: bp 110–130 °C/1.1 mmHg (bath temperature). ^{1}H NMR (C_6D_6): δ 0.30 (s, 12H), 1.04 (t, J = 7.0 Hz, 12H), 2.87 (q, J = 7.0 Hz, 8H). Anal. Calcd for $C_{12}H_{32}N_2Si_2$: C, 55.31; H, 12.38. Found: C, 55.08; H, 12.49.

When the reaction mixture was refluxed, the coupling reaction was completed in 6 h, as monitored by the disappearance of the starting material by GLC. A similar work-up gave pure **2a** in 74% yield. Alternatively, when the reaction flask was immersed in a ultrasound cleaning bath (Iwaki Glass Co., Ltd., 120W, 38 kHz) filled with water, the coupling reaction was completed in 13 h, during which time the bath temperature rose up to 50 °C. The product **2a** was obtained in rather low yield (40–50%) and in low purity (70–80%) contaminated with several unknown impurities, leaving substantial amounts of nonvolatile distillation residue.

Other disilanes were prepared in essentially the same manner as described for the synthesis of **2a** at room temperature. Note: Under reflux conditions, **2b**, **2c**, and **6** were obtained only in low yields (<50%) and in low purities.

1,2-Bis(diethylamino)-1,1,2,2-tetraisopropyldisilane (2b). This compound was obtained in 85% yield from **1b** by stirring with lithium at room temperature for 24 h. bp 120–160 °C/0.50 mmHg (bath temperature). ^{1}H NMR (C_6D_6): δ 1.08 (t, J = 7.0 Hz, 12H), 1.16–1.38 (m, 28H), 3.00 (q, J = 7.0 Hz, 8H). Anal. Calcd for $C_{20}H_{48}N_2Si_2$: C, 64.44; H, 12.98. Found: C, 64.14; H, 13.22.

1,2-Bis(diethylamino)-1,2-di-*n*-hexyl-1,2-dimethyldisilane (2c). This compound was obtained in 60% yield from **1c** by stirring with lithium at room temperature for 36 h as a nearly 1:1 mixture of *meso* and *dl* stereoisomers. bp 130–135 °C/0.80 mmHg. ^{1}H NMR (C_6D_6): δ 0.37 (s, 6H), 0.38 (s, 6H), 0.70-1.02 (m, 10H), 1.09 (t, J = 7.0 Hz, 12H), 2.93 (q, J = 7.0 Hz, 8H), 1.30–1.70 (m,

16H). Anal. Calcd for $C_{22}H_{52}N_2Si_2$: C, 65.92; H, 13.08. Found: C, 65.79; H, 13.35.

1,1,2,2-Tetrakis(diethylamino)-1,2-dimethyldisilane (6). This compound was obtained from **5** in 76% yield after 96 h-stirring. bp 110–130 °C/1.0 mmHg (bath temperature). ^{1}H NMR (C_6D_6): δ 0.39 (s, 6H), 1.10 (t, J = 7.0 Hz, 24H), 3.00 and 3.01 (dq, J = 7.0 Hz, 16H). Anal. Calcd for $C_{18}H_{46}N_4Si_2$: C, 57.69; H, 12.37. Found: C, 57.76; H, 12.61.

Preparation of 1,2-Dichloro-1,1,2,2-tetramethyldisilane (3a). Freshly distilled benzoyl chloride (0.32 mL, 2.76 mmol) was added dropwise to **2a** (388 mg, 1.38 mmol) at 0 °C over 2 min. After being stirred at 0 °C for 1 h, the mixture was distilled bulb-to-bulb to give 205 mg (80% yield) of **3a**:[3] bp 120–130 °C/90 mmHg (bath temperature). ^{1}H NMR (C_6D_6): δ 0.37 (s, 12H).

Preparation of 1,2-Dichloro-1,1,2,2-tetraisopropyldisilane (3b). By acetyl chloride: To a solution of **2b** (385 mg, 1.03 mmol) in dichloromethane (1 mL) was added freshly distilled acetyl chloride (1.50 mL, 20.7 mmol) at 0 °C and the mixture was stirred at room temperature for 3 h. After evaporation of the solvent N,N-dimethylacetamide was removed under reduced pressure up to 130 °C/28 mmHg by bulb-to-bulb distillation. The residue was further distilled bulb-to-bulb to give 294 mg (purity 90%, 85% yield) of **3b**:[17] bp 115–135 °C/0.60 mmHg (bath temperature). ^{1}H NMR (C_6D_6): δ 1.16 (d, J = 5.8 Hz, 24 H), 1.20–1.35 (m, 4H). Anal. Calcd for $C_{12}H_{28}Si_2Cl_2$: C, 48.14; H, 9.43. Found: C, 47.91; H, 9.63.

By dry HCl: Through a solution of **2b** (395 mg, 1.06 mmol) in dry THF (10 mL) was bubbled dry hydrogen chloride, generated from ammonium chloride (6.9 g, 127 mmol) and conc. sulfuric acid (4.8 mL, 85 mmol), at 0 °C for 40 min with stirring. White salts precipitated almost immediately. GLC analysis showed the disappearance of **2b**. The mixture was diluted with dry hexane (10 mL) and filtered with suction. The filtrate was concentrated and the residue was purified by

bulb-to-bulb distillation at 110–120 °C/1.0 mmHg (bath temperature) to give 270 mg (purity 95%, 80% yield) of **3b**.

Preparation of 1,2-Dichloro-1,2-di-*n*-hexyl-1,2-dimethyldisilane (3c). By dry HCl: Dry hydrogen chloride was passed through a solution of **2c** (1.09 g; 2.45 mmol) in dry ether (15 mL) at 0 °C for 1 h. Similar work-up to the above followed by bulb-to-bulb distillation (125–145 °C/0.90 mmHg, bath temperature) gave rather impure **3c**[18] as a nearly 1:1 *meso/dl* mixture in moderate yield (674 mg, purity 65%, 55% yield estimated). ^{1}H NMR (C_6D_6): δ 0.49 (s, 6H), 0.51 (s, 6H), 0.89-0.99 (m, 10H), 1.25–1.55 (m, 16H). Use of THF as solvent resulted in the lowering of the yield due to the formation of a more complex mixture.

Preparation of 1,2-Diethoxy-1,2-di-*n*-hexyl-1,2-dimethyldisilane (4c). To a suspension of ammonium chloride (51 mg; 0.94 mmol) in dry ethanol (5.0 mL) was added **2c** (710 mg; 95% pure; 1.68 mmol) at room temperature and the mixture was stirred for 2 h. Excess ethanol and the resulting diethylamine were removed under reduced pressure and the residue was diluted with dry hexane and filtered. The filtrate was concentrated and then distilled bulb-to-bulb to give 560 mg (purity 90%, 87% yield) of **4c**: bp 128–148 °C/0.8 mmHg (bath temperature). ^{1}H NMR (C_6D_6): δ 0.40 (s, 6H), 0.85–1.00 (m, 10H), 1.23 (t, J = 6.9 Hz, 6H), 1.30–1.70 (m, 16H), 3.71 (q, J = 6.9 Hz, 4H). Anal. Calcd for $C_{18}H_{42}O_2Si_2$: C, 62.36; H, 12.21. Found: C, 62.11; H, 12.34.

Preparation of 1,1,2,2-tetraethoxy-1,2-dimethyldisilane (7). In a similar manner to the above, **6** (348 mg, 0.93 mmol) gave 200 mg (87% yield) of **7**:[3] bp 50–60 °C/0.7 mmHg (bath temperature). ^{1}H NMR (C_6D_6): δ 0.40 (s, 6H), 1.24 (t, J = 7.0 Hz, 12H), 3.86 and 3.87 (dq, J = 7.0 Hz, 8H).

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by other route, amination of 1,1,2-trichlorotrimethyldisilane, but obtained a complex mixture of products only. The dimethylamino analog of **8** has been prepared in low yield by Hengge: Hengge, E.; Pletka, H. D.; Höfler, F. *Monatsh. Chem.* **1970**, *101*, 325.

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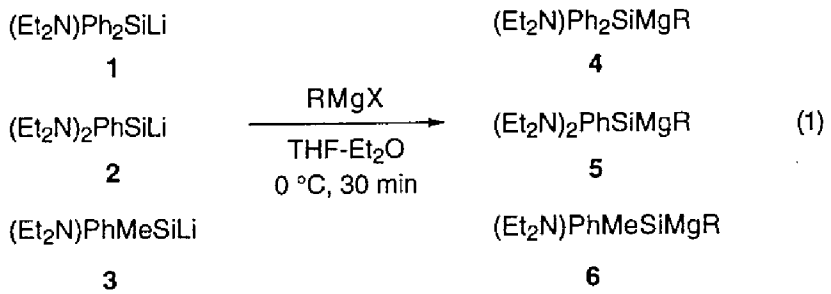
Chapter 3

Reactivity Control of Aminosilyl Anions and Synthesis of Functionalized Oligosilanes

Abstract: (Aminosilyl)(alkyl)magnesiums, which are prepared from (aminosilyl)lithiums and alkyl Grignard reagents, are useful silylating reagents for Si-Si bond elongation reactions. Competing cleavage of the Si-Si bond encountered with (aminosilyl)lithiums is suppressed. Synthesis of functionalized oligosilanes has been achieved by use of the magnesium reagents.

Introduction

As described in Chapter 1, the (aminosilyl)lithiums **1** - **3** are very useful for the synthesis of disilanes and trisilanes via coupling with chloro-monosilanes.[1] However, in reactions of the (aminosilyl)lithiums with chloro-oligosilanes, cleavage of the Si-Si bond often occurs to lower the yields of the desired coupling products. To solve this problem, the author intended to control the reactivity of aminosilyl anions by converting the counter cation (Li^+) into other metals. Considering from the electronegativity,[2] Mg (1.23), Zn (1.66), and Cu (1.75) are expected to make more covalent bonding to Si (1.74) than Li (0.97), so that the reactivity of silylmagnesium, silylzinc, and silylcopper[3] will be different from that of silyllithium. Among those metals so far examined, it was found that (aminosilyl)(alkyl)magnesiums **4** - **6** are most suitable for the purpose. Described herein are the development of (aminosilyl)(alkyl)magnesiums and its application to the synthesis of functionalized oligosilanes.[4]



(1)

Results and Discussion

The (aminosilyl)(alkyl)magnesiums **4** - **6** can be prepared in situ by mixing (aminosilyl)lithiums **1** - **3** with alkyl Grignard reagents (RMgX) at 0 °C, based on the report by Hiyama, Oshima, Nozaki, and their coworkers (eq. 1).[5] Potentially, **4** - **6** offer two types of reactions, that is, silylation and alkylation. The transfer ability of silyl group and alkyl group on **4** toward $PhMe_2SiCl$ was examined (Scheme 1). Selectivity of silylation increases as alkyl group becomes bulkier: When R is the isopropyl group, alkylation is suppressed completely. All the three (aminosilyl)(isopropyl)magnesiums exhibit a sufficient reactivity toward chlorosilanes to afford disilanes in good yield without formation of isopropylsilanes (Scheme 2). It should be noted that the coupling reactions regenerate the isopropyl Grignard reagent as by-product. Therefore, it was necessary for isolation of the (amino)disilanes to decompose the Grignard reagent keeping the aminosilane functionality intact. The author found that hydrolysis under a rather strongly alkaline condition using 1 M NaOH aq. at 0 °C was suitable for this purpose.

Another significant aspect is that the undesired Si-Si bond cleavage has been almost completely suppressed by the silylmagnesium reagent, when applied to further Si-Si bond elongation reactions, as shown in Scheme 3. Reaction of 2 equiv of **4** with a 1,1-dichlorodisilane **11** afforded the desired coupling product in higher than 95% chemoselectivity, while the lithium reagent **1** caused the Si-Si bond cleavage considerably, forming **13** in *ca.* 15% selectivity.

Scheme 1

$(Et_2N)Ph_2SiMgR$ + $PhMe_2SiCl$ → (0 °C, 30 min and room temp., overnight)

4

$(Et_2N)Ph_2Si$-$SiMe_2Ph$ + R-$SiMe_2Ph$

7 **8**

RMgX in eq 1		total yield[a]	silylataion (**7**)		alkylation (**8**)[b]
R = Me	X = Br	80%	87	:	13
Et	Br	80%	87	:	13
i-Pr	Br or Cl	76–80%	100	:	0

[a] Isolated yields by bulb-to-bulb distillation.

[b] The ratio was determined by ^1H NMR analysis of the reaction mixture.

Scheme 2

$(Et_2N)_nPh_{3-n}SiMg$*i*-Pr + $PhMe_2SiCl$ → (0 °C, 0.5–1.5 h)

4 (n = 1)
5 (n = 2)

$(Et_2N)_nPh_{3-n}Si$-$SiMe_2Ph$ + (*i*-PrMgCl)

7 (n = 1) 80%
9 (n = 2) 72%

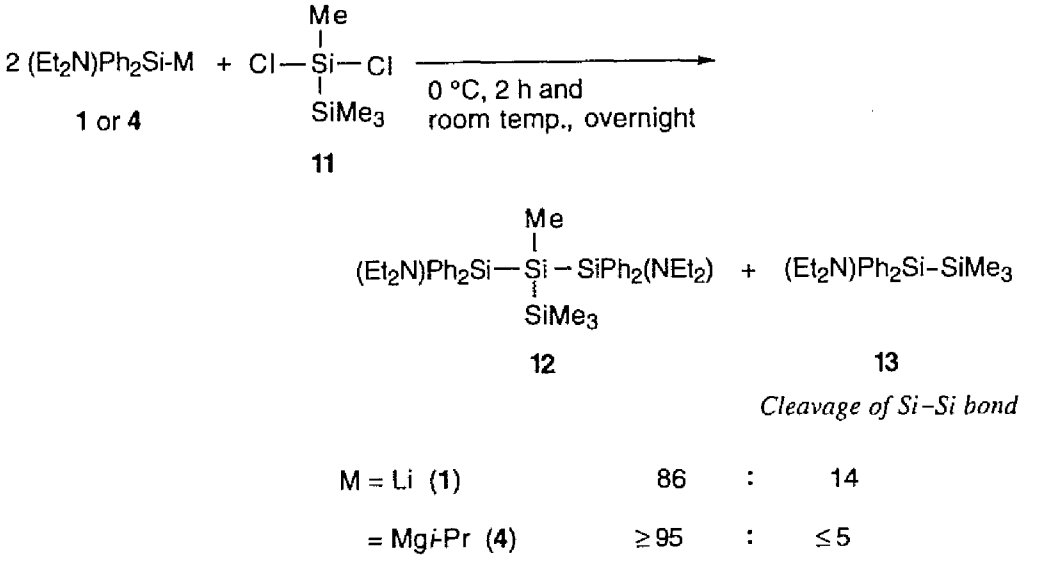
$(Et_2N)PhMeSiMg$*i*-Pr + $PhMe_2SiCl$ → (0 °C, 0.5 h)

6

$(Et_2N)PhMeSi$-$SiMe_2Ph$ + (*i*-PrMgCl)

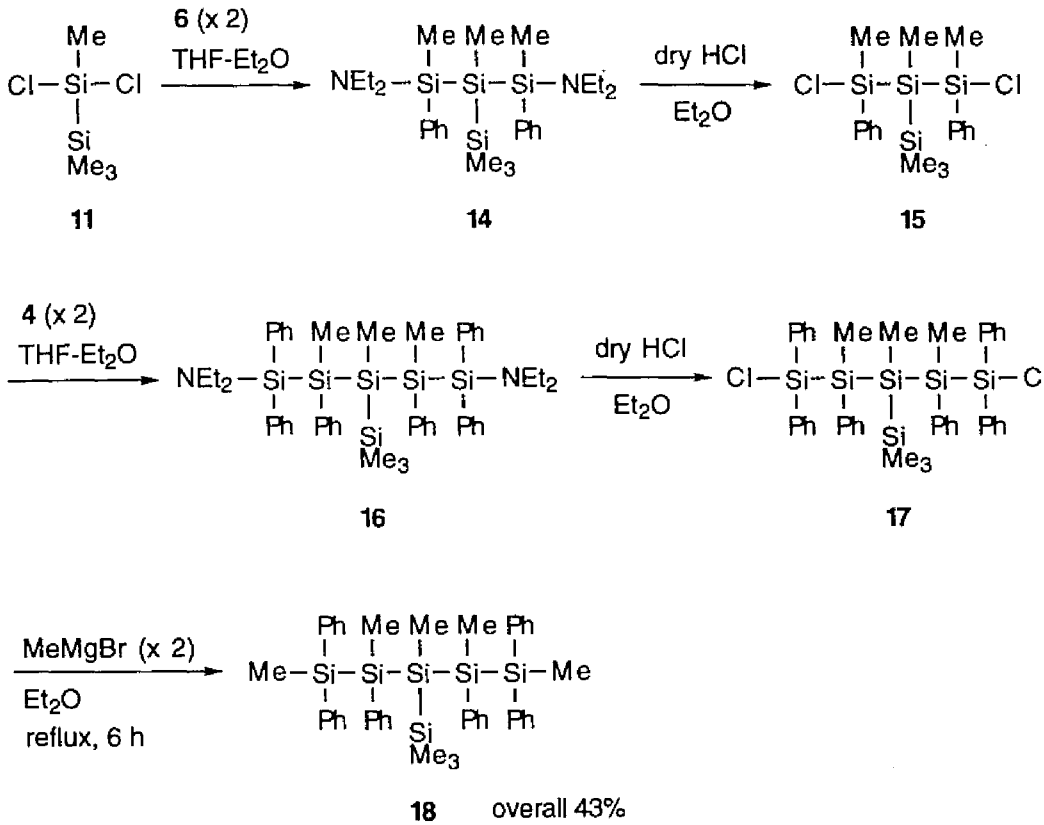
10 ~ 50%

Scheme 3



Synthesis of functionalized oligosilanes[4] by using this methodology has been achieved as shown in Scheme 4. Reaction of **6** (2 equiv) with 1,1-dichlorodisilane **11** in THF-Et_2O afforded the desired bis-silylated product, 1,3-bis(diethylamino)tetrasilane **14.** The amino groups of **14** were converted into chlorines by treatment with dry HCl[6] in Et_2O at room temperature to yield **15.** ^{29}Si NMR spectra of **15** showed signals at 18 (Si^c), -11 (Si^a), and -77 ppm (Si^b), which strongly support the branced structure (Figure 1). Further silylation of **15** was achieved by use of **4** (2 equiv) to afford 1,6-bis(diethylamino)hexasilane **16.** Chlorination of **16** and subsequent methylation of the resulting **17** gave the branched hexasilane **18** in 43% overall yield. ^{29}Si NMR spectra of **18** showed signals at -11 (Si^A), -19 (Si^D), -39 (Si^C) and -76 (Si^B) ppm, which support the branched structure (Figure 1). The results demonstrate that further Si-Si bond elongation will be achieved in principle by the reiterative silylation and chlorination.

Scheme 4



11 **14** **15**

16 **17**

18 overall 43%

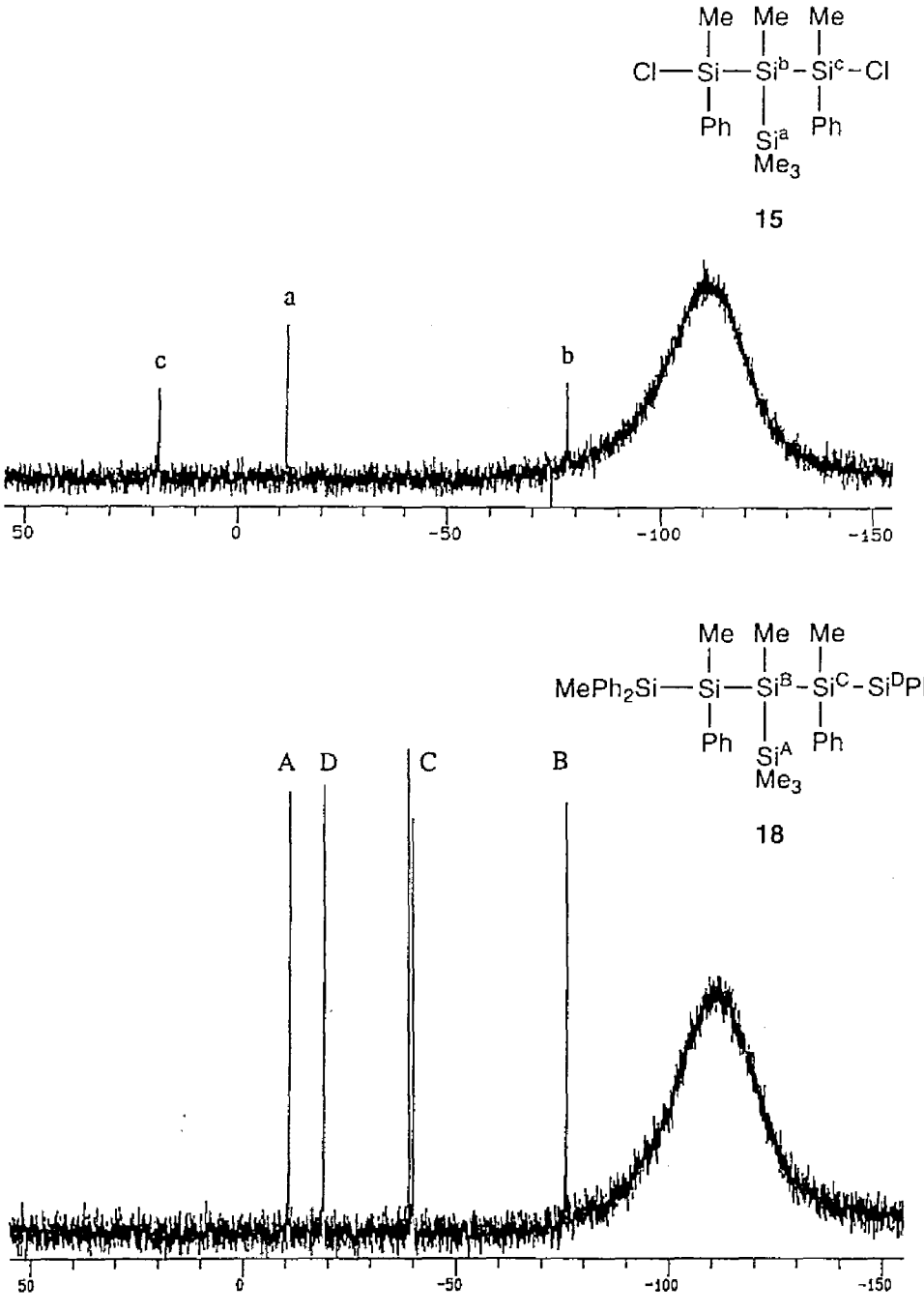


Figure 1. ^{29}Si NMR spectra of **15** and **18**

Experimental Section

General Remarks. ^{1}H (200 MHz), ^{13}C (50.29 MHz), and ^{29}Si (39.73 MHz) NMR spectra were recorded on a Varian VXR-200 spectrometer or ^{1}H (270 MHz), ^{13}C (67.94 MHz), and ^{29}Si (53.67 MHz) NMR spectra were recorded on a JEOL EX-270 spectrometer. ^{1}H and ^{13}C chemical shifts are referenced to internal benzene-d_6 (^{1}H δ 7.200 ppm and ^{13}C δ 128.00 ppm). Mass spectra were measured on a JEOL JMS-D300 mass spectrometer connected with a JEOL LGC-20K gas chromatograph, equipped wiyh a 1-m glass column packed with OV-17 (3%) on Chromosorb. The elemental analyses were performed at the Microanalysis Center of Kyoto University: Analytical samples were purified by preparative GLC or preparative MPLC. GLC analysis was performed on a Shimadzu GC-4B gas chromatographed, equipped with 3-m or 1-m column packed with 30% Silicone DC550 on Celite 545. Column chromatography was performed by using Kieselgel 60 (70–230 mesh) (Merck). Thin layer chromatography (TLC) was performed on plates of silica gel 60F-254 (Merck). Preparative medium pressure liquid chromatography (MPLC) was performed with a silica gel prepacked C.I.G. (Si-10) column (Kusano).

1,1-Dichlorotetramethyldisilane was prepared by the literature method.[7] Phenyldimethylchlorosilane was distilled at reduced pressure before use. Lithium dispersion (25 wt. % in mineral oil) was purchased from Aldrich. Lithium granular was purchased from Chemetall Gesellshaft. Ether and THF were distilled under nitrogen from sodium/benzophenone. Hexane was dried over sodium wire and distilled under nitrogen. All reactions were carried out under a nitrogen atmosphere.

Typical Procedure: Preparation of [Bis(diethylamino)phenylsilyl](isopropyl)magnesium (5) and Trapping as 1,1-Bis(diethylamino)-1,2-diphenyl-2,2-dimethyldisilane (9). To a solution of **2**, which was prepared from bis(diethylamino)phenylchlorosilane (1.97 mmol) and lithium dipersion (11 mg-atom) in THF (4.0 mL), was added *i*-PrMgBr in Et_2O (1.49 mL, 1.97 mmol) over 1 min at 0 °C and the solution was stirred for 30 min to

afford a dark brown solution of **5**. To the solution was added phenyldimethylchlorosilane (0.358 mL, 2.17 mmol) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C and overnight at room temperature. The reaction mixture was diluted with hexane (20 mL), stirred vigorously, and filtered. The filtrate was concentrated and the residue was subjected to bulb-to-bulb distillation to give **9** (543 mg, 72% yield) as pale yellow oil. bp 185–205 °C/0.55 mmHg (bath temperature). ^{1}H NMR (C_6D_6): δ 0.53 (s, 6H), 1.01 (t, J = 7.0 Hz, 12H), 3.02 (q, J = 7.0 Hz, 8H), 7.18–7.22 (m, 3H), 7.29–7.33 (m, 3H), 7.46–7.50 (m, 2H), 7.71–7.75 (m, 2H). ^{13}C NMR (C_6D_6): δ –1.28, 15.03, 40.24, 127.82, 127.95, 128.60, 129.15, 134.72, 135.52, 139.51, 140.23. MS: *m/e* 384 (M^+). Anal. Calcd for $C_{22}H_{36}N_2Si_2$: C, 68.69; H, 9.43. Found: C, 68.60; H, 9.26.

Procedure for Aqueous Workup. To decompose the regenerated isopropyl Grignard reagent keeping the aminosilane functionality intact, the following basic aqueous workup was effective for the case of **7** and **9**: The reaction mixture (containing about 2 mmol of the Grignard reagent) was filtered. To the filtrate was added slowly a 1 M NaOH aq. solution (1.0 mL) at 0 °C and the mixture was stirred at 0 °C ca. 10 min. The mixture was filtered and the filtrate was dried over K_2CO_3 and concentrated to afford **7** or **9** without significant decomposition.

1-Diethylamino-1,1,2-triphenyl-2,2-trimethyldisilane (7). bp 225–255 °C/1.0 mmHg (bath temperature). ^{1}H NMR (C_6D_6): δ 0.25 (s, 9H), 1.00 (t, J = 7.0 Hz, 6H), 3.03 (q, J = 7.0 Hz, 4H), 7.26–7.30 (m, 3H), 7.71–7.76 (m, 2H). ^{13}C NMR (C_6D_6): δ –1.99, 15.28, 41.86, 127.93, 128.07, 128.85, 129.28, 134.74, 135.71, 138.12, 139.21. MS: *m/e* 389 (M^+). Anal. Calcd for $C_{24}H_{31}NSi_2$: C, 73.77; H, 8.01. Found: C, 73.54; H, 8.10.

1-Diethylamino-1,2-diphenyl-1,2,2-trimethyldisilane (10). bp 160–180 °C/1.0 mmHg (bath temperature). ^{1}H NMR (C_6D_6): δ 0.42 (s, 3H), 0.44 (s, 3H), 0.52 (s, 3H), 0.92 (t, J = 7.0 Hz, 6H), 2.87 (q, J = 7.0 Hz, 4H), 7.23–7.29 (m, 6H), 7.47–7.52 (m, 2H), 7.58–7.62 (m, 2H). ^{13}C NMR (C_6D_6): δ

-2.91, -1.72, 15.71, 41.69, 128.00, 128.07, 128.74, 128.99, 134.42, 134.54, 139.54, 140.35. MS: *m/e* 327 (M^+). Anal. Calcd for $C_{19}H_{29}NSi_2$: C, 69.66; H, 8.92. Found: C, 69.36; H, 9.19.

Reaction of [(Diethylamino)diphenylsilyl](isopropyl)magnesium (4) with 1,1-Dichlorotetramethyldisilane (11): Synthesis of 2-Trimethylsilyl-1,3-bis(diethylamino)-1,1,3,3-tetraphenyl-2-methyltrisilane (12). To a solution of **1** (12.2 mmol) in THF (24 mL) was added *i*-PrMgBr in Et_2O (9.23 mL, 12.2 mmol) over 7 min at 0 °C. The reaction solution was stirred at 0 °C for 30 min. To the solution was added a solution of **11** (purity 96%, 1.02 g, 5.21 mmol) in Et_2O (1.0 mL) at 0 °C over 3 min. The reaction mixture was stirred at 0 °C for 2 h and at room temperature overnight. To the reaction mixture was added slowly 1 M NaOH aq. solution (0.66 mL) at 0 °C and stirred for a while. The mixture was filtered and the filtrate was dried over K_2CO_3 and concentrated in vacuo to give a mixture of **12** and **13**: ^{1}H NMR analysis of the mixture showed that the ratio of **12/13** was ≥95/≤5. **12:** ^{1}H NMR (C_6D_6): δ 0.14 (s, 9H), 0.66 (s, 3H), 0.94 (t, J = 7.0 Hz, 12H), 3.00 (q, J = 7.0 Hz, 8H), 7.23-7.27 (m, 12H), 7.60-7.64 (m, 4H), 7.69-7.74 (m, 4H). **13:** ^{1}H NMR (C_6D_6): δ 0.25 (s, 9H), 1.00 (t, J = 7.0 Hz, 6H), 3.03 (q, J = 7.0 Hz, 4H), 7.26-7.30 (m, 6H), 7.71-7.75 (m, 4H).

Reaction of [(Diethylamino)diphenylsilyl]lithium (1) with 11. To a solution of **1** (2.15 mmol) in THF (3.0 mL) and Et_2O (1.6 mL) was added a solution of **11** (purity 96%, 252 mg, 0.97 mmol) in Et_2O (1.0 mL) at 0 °C and the reaction solution was stirred at 0 °C for 2 h and at room temperature overnight. The reaction mixture was evaporated and the residue was diluted with hexane (10 mL) and filtered. The filtrate was concentrated in vacuo to give a mixture of **12** and **13**: ^{1}H NMR analysis of the mixture showed that the ratio of **12/13** was 86/14.

Synthesis of 3-Trimethylsilyl-1,1,2,4,5,5-hexaphenyl-1,2,3,4,5-pentamethylpentasilane (18). (1) To a solution of **3**, which was prepared from

(diethylamino)phenylmethylchlorosilane (11.8 mmol) and lithium dipersion (48.5 mg-atom) in THF (24 mL), was added *i*-PrMgBr in Et_2O (8.93 mL, 11.8 mmol) over 5 min at 0 °C and the solution was stirred for 30 min to afford a dark brown solution of **6**. To the solution was added **11** (96% pure, 856 mg, 4.37 mmol) in THF (2.0 mL) at 0 °C. The reaction mixture was stirred for 2 h at 0 °C and overnight at room temperature. The reaction mixture was diluted with hexane (30 mL), stirred vigorously, and filtered. The filtrate was concentrated in vacuo to give crude **14** (2.36 g) as colorless oil, which was used in the next step without purification.

(2) Through a solution of **14** (2.36 g) in Et_2O (30 mL) was bubbled dry hydrogen chloride, generated from ammonium chloride (16.6 g, 306 mmol) and concentrated sulfuric acid (13.1 mL, 236 mmol), at 0 °C for 1 h with stirring. The mixture was diluted with hexane (30 mL) and filtered. The filtrate was concentrated to afford crude **15** (1.77 g) as oil, which was used in the next step without purification.; **2-Trimethylsilyl-1,3-dichloro-1,3-diphenyl-1,2,3-trimethyltrisilane (15):** ^{29}Si NMR (C_6D_6): δ 18.9, 18.8, 18.6, 18.4, -11.5, -77.9.

(3) Solution of **4**, which was prepared from **1** (2.05 mmol) in THF (3.5 mL) and *i*-PrMgBr in Et_2O (1.55 mL, 2.05 mmol), was added to a solution of **15** (382 mg, about 0.89 mmol) in THF (5.0 mL) at 0 °C over 20 min and the reaction solution was stirred at 0 °C for 12 h and at room temperature overnight. To the solution was added 1 M NaOH aq. solution (0.11 mL) at 0 °C and the mixture was stirred at 0 °C for 5 min . The mixture was dried over K_2CO_3 and concectrated to give crude **16** (832 mg) as oil, which was used in the next step without purification.

(4) Through a solution of **16** (832 mg) in Et_2O (10 mL) was bubbled dry hydrogen chloride, generated from ammonium chloride (7.25 g, 134 mmol) and concentrated sulfuric acid (6.00 mL, 108 mmol), at 0 °C for 40 min with stirring. The mixture was diluted with hexane (20 mL) and filtered. The filtrate was concentrated to afford crude **17** as oil, which was used in the next step without purification.

(5) To a solution of **17** in Et_2O (4.0 mL) was added MeMgBr in Et_2O (1.45 mL, 4.10 mmol) at room temperature over 5 min and the reaction mixture was stirred

at room temperature for 30 min and refluxed for 6 h. After being cooled to 0 °C, the reaction mixture was hydrolyzed with 1 M hydrochloric acid (10 mL) and extracted with Et_2O (20 mL x 2). The combined organic layer was washed with brine (10 mL), water (10 mL), and dried over $MgSO_4$, and concentrated. The residue was subjected to column chromatography on silica gel (30 mL) eluted with hexane/AcOEt (40/1) to give crude **18** (497 mg, $R_f = 0.28$). Further purification by MPLC eluted with hexane/AcOEt (40/1) gave pure **18** (303 mg) in overall 43% yield based on **11**. ^1H NMR (C_6D_6): δ -0.01 (s, 9H), 0.28 (s, 3H), 0.41 (s, 3H), 0.51 (s, 3H), 0.51 (s, 3H), 0.68 (s, 3H), 0.69 (s, 3H), 7.08-7.22 (m, 18H), 7.26-7.29 (m, 2H), 7.34-7.43 (m, 6H), 7.48-7.57 (m, 4H). ^{13}C NMR (C_6D_6): δ -8.55, -5.39, -5.01, -3.50, -3.30, 0.49, 127.42, 127.49, 127.53, 127.62, 127.67, 127.87, 128.10, 128.48, 128.77, 128.82, 134.91, 135.11, 135.18, 135.27, 135.42, 136.68, 136.73, 137.16, 137.41, 137.52. ^{29}Si NMR (C_6D_6): δ -10.9, -18.9, -19.1, -38.9, -40.0, -76.0. MS: m/e 750 (M^+, 6), 553 (M^+-Ph, 80), 476 (M^+-$SiPh_2Me$, 35), 433 (M^+-(SiPhMe-$SiPh_2Me$), 34), 317 (29), 281 (29), 197(100), 135 (76).

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Chapter 4

Synthetic Applications of Functionalized Silyl Anions: Aminosilyl Anions as Hydroxy Anion Equivalent

Abstract: An (aminosilyl)lithium and the corresponding copper and magnesium reagents serve as a hydroxy anion equivalent through (1) allylic substitution, (2) addition to vinyloxirane, (3) addition to acetylene, and (4) conjugate addition (Michael addition), followed by oxidative cleavage of the silicon-carbon bonds. Highly regio- and stereoselective transformations have been achieved in all cases.

Introduction

Silyl anions are good nucleophiles, which undergo nucleophilic substitution with alkyl halides, allylic substitution, conjugate addition, and addition to alkynes.[1] The introduced silyl group can be converted into hydroxy group by oxidative cleavage of the silicon-carbon bond.[2] Thus, silyl anions serve as hydroxy anion equivalent.

The conventional Fleming's $PhMe_2Si$ anion chemistry[3] requires introduction of a heteroatom on silicon via cleavage of the Si-Ph bond by acid treatment before oxidative cleavage of the silicon–carbon bond. This method therefore cannot be applied to at least three types of silanes, that is, allylsilane, vinylsilane, and β-hydroxy-silane, because the acid treatment might cleave the silicon–allyl and –vinyl carbon bond much faster than the silicon–phenyl carbon bond[4] or might cause the Peterson olefination of the β-hydroxy-silane.[5] The aminosilyl anion chemistry which the author developed has afforded a solution to this problem: No acid treatment is required since the silyl group is already functionalized. Recently, Fleming et al. have found another solution to this problem by use of a well-designed (allylsilyl)lithium:[6] An allyl group, 2-methylbut-2-enyl group, on silicon can be removed selectively with very weak acids with other allyl-, vinyl-, and β-hydroxy-silane moieties intact. Taber et al. also reported quite recently that a phenyl group on

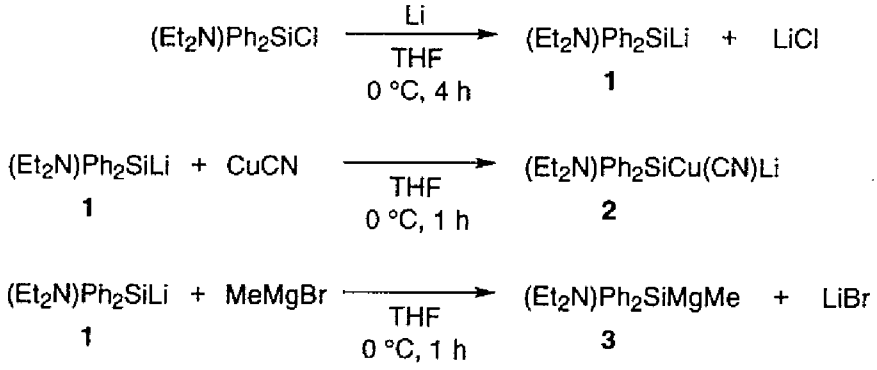
silicon can be removed in two steps under basic conditions which involve reduction with lithium/ammonia to cyclohexadienyl group followed by treatment with tetrabutylammonium fluoride.[7]

Reported herein are some examples of synthetic applications of (aminosilyl)lithium **1**, the corresponding copper reagent **2**, and the corresponding magnesium reagent **3**: regio- and stereoselective synthesis of allylsilanes, β-hydroxysilanes, and vinylsilanes and their conversion to the corresponding alcohols and aldehyde. Conjugate addition to α,β-unsaturated ester was also examined.

$(Et_2N)Ph_2SiLi$ **1** $(Et_2N)Ph_2SiCu(CN)Li$ **2** $(Et_2N)Ph_2SiMgMe$ **3**

$(Et_2N)Ph_2Si^- \equiv OH^-$

Scheme 1



Results and Discussion

1. Preparation of the reagents

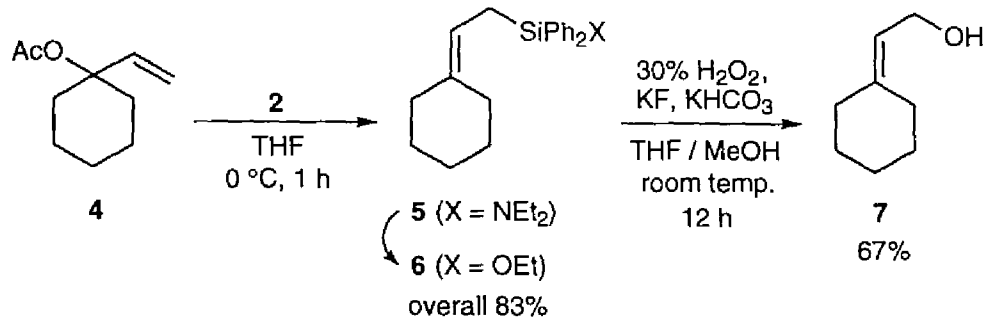
(Aminosilyl)lithium **1** was prepared from the corresponding (amino)chlorosilane with lithium metal in THF at 0 °C for 4 h in quantitative yield.[8] The copper reagent **2** and the magnesium reagent **3** were prepared from **1** with 1 equiv of copper cyanide[3] and methylmagnesium bromide[9] in THF, respectively (Scheme 1). The solutions were used without titration.

2. Allylsilane via allylic substitution

The silyl cuprate reagent **2** underwent allylic substitution reaction with 1-vinyl cyclohexyl acetate **4** to give amino-substituted [2-(cyclohexylidene)ethyl]silane **5** (Scheme 2).[10] Although the silicon-nitrogen bond of **5** could be tolerated with neutral aqueous workup, it decomposed on silica gel. For isolation, **5** was converted by ethanolysis into ethoxy derivative **6** (83% yield) which was stable on silica gel.

Conversion of the ethoxy derivative **6** into the corresponding allyl alcohol **7** was achieved by the H_2O_2 oxidation in 67% yield without cleavage of the silicon-allyl carbon bond. Direct H_2O_2 oxidation of amino derivative **5** without purification was also successful to afford **7** in 63% yield.

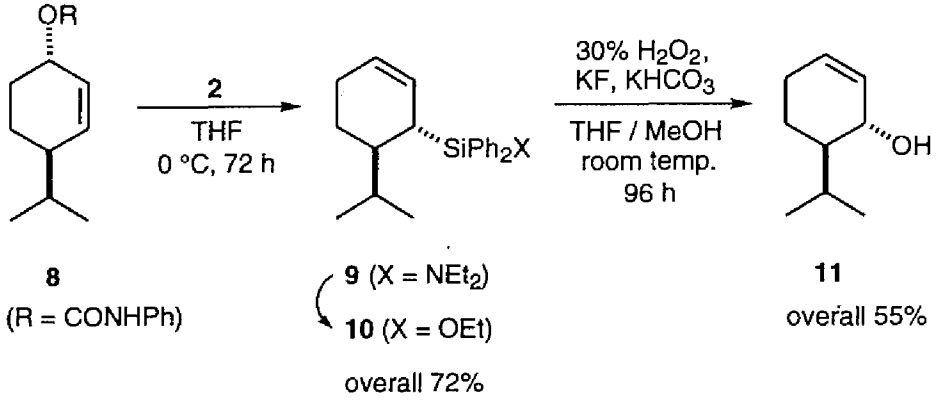
Scheme 2



Reaction of cyclohexyl carbamate **8** (R = CONHPh)[11] with **2** proceeded in an S_N 2' manner and with *syn* selectivity to the leaving group (-OR) (Scheme 3).[10] The selectivity may be explained in terms of the interaction between nitrogen of the carbamate and copper of the cuprate, as proposed for reactions with ordinary organocuprates.[12] Excess amounts of **2** (6 equiv) and longer reaction period were required as compared with the case of **4**. Ethanolysis of the resulting amino-substituted allylsilane **9** afforded ethoxy derivative **10** in 72% yield. The allylsilane **9** was converted into the corresponding allyl alcohol **11** by H_2O_2 oxidation with retention of configuration in 55% yield. The stereochemistry was confirmed by ^1H NMR data, which are the identical with authentic data.[13] The reagent **2** underwent

no substitution with an acetate (R = Ac in **8**) and a 2,4,6-trimethylbenzoate (R = 2,4,6-$Me_3C_6H_2CO$ in **8**).[14] The choice of the leaving group is thus essential, but the S_N2' replacement reaction also affords a new access to regio- and stereo-defined sila-functionalized allylsilanes, which have potential utility for organic synthesis.

Scheme 3

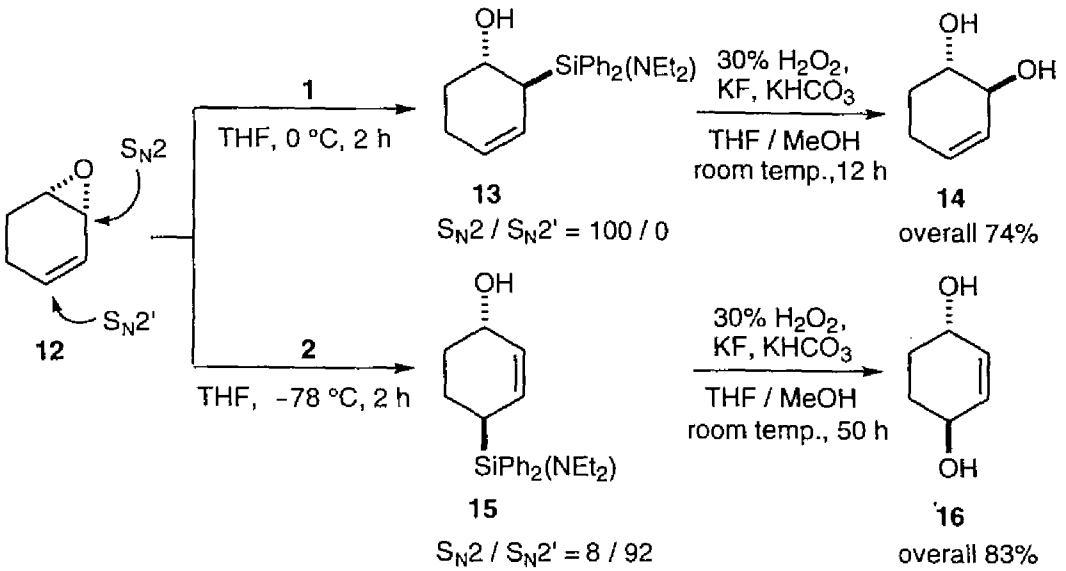


3. β-Hydroxysilane via ring-opening of epoxides

Monoepoxide of 1,3-cyclohexadiene[15] **12** can be converted into 1,2- and 1,4-diol by use of **1** and **2**, respectively, as summarized in Scheme 4.[10] The lithium reagent **1** underwent an S_N2 type ring opening reaction with **12** in a completely regio- and stereoselective fashion to give the *trans*-(β-hydroxy)silane **13** which contains an allylsilane unit also. Treatment of **13** with H_2O_2 afforded the corresponding alcohol **14** in 74% yield. The stereochemistry of **14** was confirmed by the ^1H NMR spectroscopic data, which are identical with the authentic data.[17] In contrast to this, the silyl cuprate **2** underwent an S_N2' allylic substitution reaction with **12** with high regioselectivity and complete stereoselectivity to give the *trans* product **15** which is regarded as a vinylogous β-hydroxysilane. While no *cis* product was formed at all, the regioselectivity depended on the reaction temperature. Thus, the S_N2': S_N2 ratio was 92 : 8 at −78 °C, but roughly 50 : 50 at 0 °C. The corresponding 1,4-diol **16** was obtained in 83% yield by the H_2O_2 oxidation, which required larger amounts of H_2O_2 and longer reaction period than the oxidation of

13. The stereochemistry of **16** was also confirmed by the ^{1}H NMR spectroscopic data, which are identical with the authentic data.[17]

Scheme 4

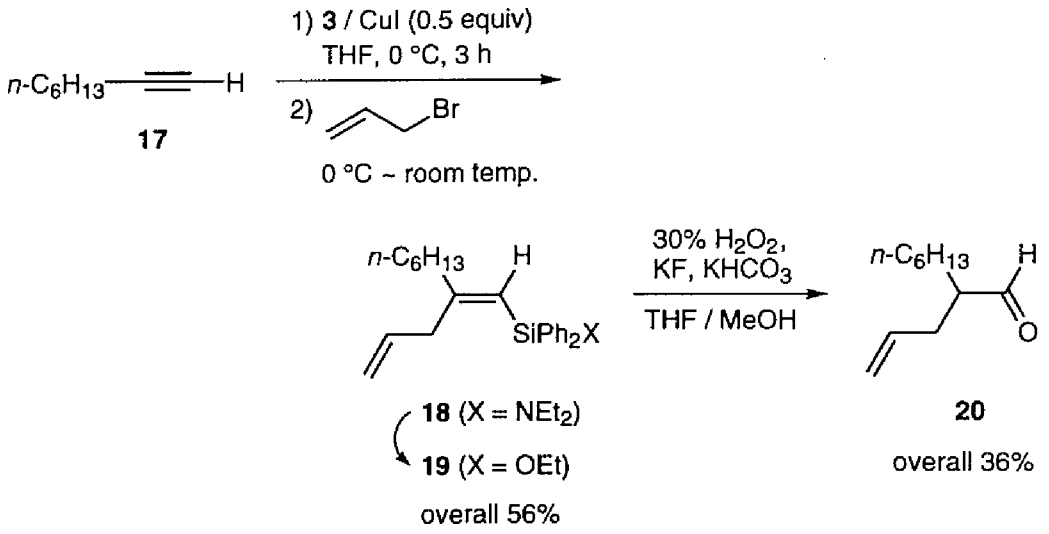


4. Vinylsilane by addition to alkyne

Addition of silyl anions to alkynes is one of the well-established routes to vinylsilanes.[18] For example, silylcuprate $(Me_2PhSi)_2Cu(CN)Li_2$ has been reported to undergo addition to 1-alkynes in a highly regioselective fashion to carry the silyl group onto the terminal carbon.[18] It has also been reported that a silylmagnesium reagent prepared from $MePh_2SiLi$ and MeMgI underwent a similar regioselective addition to alkynes in the presence of a catalytic amount of CuI.[10] In the present cases, however, addition of the (aminosilyl)cuprate **2** to 1-alkyne **17** occurred with low regioselectivity, together with deprotonation. The observed deprotonation makes a sharp contrast to the fact that the Fleming's $(Me_2PhSi)_2Cu(CN)Li_2$ does not remove the proton from 1-alkyne.[18] Stereo- and regioselective addition to the 1-alkyne was achieved by the (aminosilyl)magnesium reagent **3** in the presence of 0.5 equiv of CuI to give vinylsilane **18** after trapping with allyl bromide (Scheme 5). The use of at least 0.5 equiv of CuI was essential to prevent the deprotonation. The

amino derivative **18** was converted into **19** by ethanolysis for characterization. Direct treatment of **18** with H_2O_2 afforded the corresponding aldehyde[19] **20** in overall 36% yield.

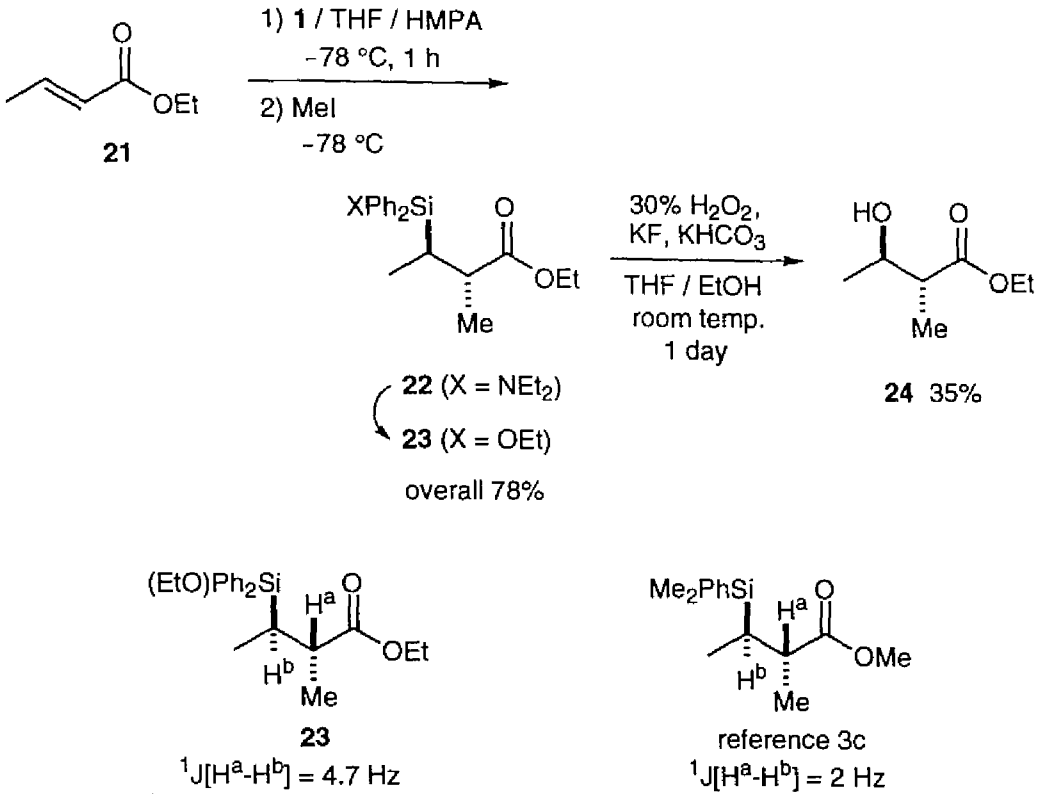
Scheme 5



5. β-Silyl ester by conjugate addition

The (aminosilyl)lithium **1** underwent conjugate addition to α,β-unsaturated ester **21** (Scheme 6).[3] The trapping of the resulting enolate with MeI gave **22** as the *anti* isomer only, which was converted into ethoxy derivative **23** in 78% yield. The *anti* selectivity is consistent with the results observed in the $PhMe_2Si$ anion chemistry.[3] The silyl group of **23** was converted into hydroxy group with skip of acid treatment to give β-hydroxy ester **24** in 35% yield. The stereochemistry was determined by the coupling constant of **23**, which was similar to the reported value.[3c]

Scheme 6



Experimental Section

General Remarks. ^{1}H (200 MHz), ^{13}C (50.29 MHz) NMR spectra were recorded on a Varian VXR-200 spectrometer. ^{1}H and ^{13}C chemical shifts are referenced to internal benzene-d_6 (^{1}H δ 7.200 ppm and ^{13}C δ 128.00 ppm) or $CDCl_3$ (^{13}C δ 77.00 ppm). Mass spectra were recorded on a JEOL JMS-D300 mass spectrometer. Melting points were measured with a Yanaco-MP-S3 apparatus. The elemental analyses were performed at the Microanalysis Center of Kyoto University: Analytical samples were purified by recrystallization, preparative GLC, or preparative MPLC. Column chromatography was performed by using Kieselgel 60 (70-230 mesh) (Merck). Thin layer chromatography (TLC) was performed on plates of silica gel 60F-254 (Merck). Preparative medium pressure liquid

chromatography (MPLC) was performed with a silica gel prepacked C.I.G. (Si-10) column (Kusano).
Lithium granular was purchased from Chemetall Gesellshaft. Spray-dried KF was purchased from Wako Pure Chemical Industries. THF was distilled under nitrogen from sodium/benzophenone. Hexane was distilled under nitrogen from sodium. Ethanol was distilled from magnesium ethoxide. Copper(I) cyanide was dried by azeotropic distillation with dry toluene (1 - 3 mL) two or three times. All reactions were carried out under a nitrogen atmosphere.

Preparation of [(Diethylamino)diphenylsilyl]lithium (1). To a mixture of lithium granular (397 mg, 57.2 mg-atom) and THF (7.0 mL) was added dropwise (diethylamino)diphenylchlorosilane (4.24 g, 14.6 mmol) with stirring at room temperature over 5 min. An exothermic reaction started in a few minutes and then THF (7.0 mL) was added. After about 20 min, the solution turned blue. The mixture was then cooled to 0 °C and stirred for 4 h, resulting in the formation of a dark green solution of **1** in quantitative yield. The solution was used without titration.

Typical Procedure for Preparation of Lithium [(Diethylamino)diphenylsilyl](cyano)cuprate (2) and Synthesis of [2-(Cyclohexylidene)ethyl](diethylamino)diphenylsilane (5). To a suspension of copper(I) cyanide (purity >90%, 1.47 g, 14.7 mmol) in THF (7.0 mL) was added the whole solution of **1**, prepared above, via a syringe over a few minutes: The mixture was stirred at 0 °C for 1 h. The resulting black solution of **2** was cooled at −20 °C and 1-vinylcyclohexyl acetate **4** (1.70 g, 10.1 mmol) was added over 3 min. After being stirred at −20 °C for 5 min and at 0 °C for 1 h, the reaction was quenched by addition of a 5% aq. solution of NH_4Cl (30 mL). The mixture was filtered and the filtrate was extracted with ether (30 mL x 3). The combined organic layer was washed several times with a 5% aq. solution of NH_4Cl (20 mL each) for the purpose of complete removal of copper salts from the organic layer until the aqueous layer became colorless, followed by washing with brine (20

mL) and drying over Na_2SO_4. Filtration and evaporation of solvent gave crude **5** as a yellow oil, which is used in the next oxidation step without purification. ^1H NMR (C_6D_6): δ 1.00 (t, J = 7.0 Hz, 6H), 1.25-1.60 (m, 6H), 2.00-2.13 (m, 4H), 2.19 (d, J = 8.4 Hz, 2H), 2.97 (q, J = 7.0 Hz, 4H), 5.42 (m, 1H), 7.26-7.31 (m, 6H), 7.72-7.77 (m, 4H).

Hydrogen Peroxide Oxidation of 5: Synthesis of 2-(Cyclohexylidene)ethyl alcohol (7). A flask was charged with the crude **5** obtained above, followed by successive addition of THF (15.0 mL), methanol (15.0 mL), KF (6.10 g, 105 mmol; 7.2 molar equiv to the aminochlorosilane), $KHCO_3$ (5.89 g, 58.5 mmol; 4 molar equiv to the aminochlorosilane). To the stirring mixture was added dropwise 30% H_2O_2 (7.4 mL, 65.5 mmol; 4.5 molar equiv to aminochlorosilane) via pipet over 10 min at room temperature. A somewhat cloudy organic layer and a milky-white heavy inorganic layer resulted. An exothermic reaction started during the addtion to raise the temperature up to 40 °C and ceased in about 30 min. The mixture was stirred at room temperature for 6 h and at 35 - 40 °C for another 6 h. After cooling to room temperature, the mixture was poured into water (50 mL) and the insoluble white precipitates were removed by decantation. The liquid phase was extracted with Et_2O (30 mL x 5). The combined organic layer was washed successively with 10% aq. solution of $Na_2S_2O_3$ (50 mL), a 1 M aq. solution of NaOH (30 mL x 3), and water, and then dried over $MgSO_4$. After filtration and evaporation of solvent, the residue was subjected to column chromatography on silica gel eluted with hexane/AcOEt (7/1) to give **7** (798 mg, 63% overall yield based on **4**) (R_f = 0.18) as a colorless oil. ^1H NMR ($CDCl_3$): δ 1.20-1.35 (broad, 1H), 1.42-1.65 (m, 6H), 2.02-2.25 (m, 4H), 4.13 (d, J = 7.1 Hz, 2H), 5.35 (tt, J = 7.1 and 1.1 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 26.66, 27.85, 28.37, 28.82, 37.02, 58.54, 120.21, 144.53. IR (neat): cm^{-1} 3340, 2930, 2860, 1670, 1450, 1060, 995.

Typical Procedure for Conversion of Diethylamino Group into Ethoxy Group: [2-(Cyclohexylidene)ethyl](ethoxy)diphenylsilane (6).

To the crude **5**, which was prepared from 3.8 mmol of **4**, and NH_4Cl (103 mmg, 1.9 mmol) was added ethanol (5.0 mL) at room temperature and stirred for 24 h. The volatile materials were removed at reduced pressure. The residue was diluted with hexane (20 mL), filtered, and the residue was evaporated. The remaining oil was subjected to column chromatography on silica gel (50 mL) eluted with hexane/AcoEt (100/1) to give **6** (1.07 g, $R_f = 0.29$) in 83% yield (based on **4**). ^1H NMR (C_6D_6): δ 1.17 (t, J = 7.0 Hz, 3H), 1.22-1.35 (m, 3H), 1.35-1.50 (m, 4H), 2.00-2.07 (m, 4H), 2.19 (d, J = 8.1 Hz, 2H), 3.74 (q, J = 7.0 Hz, 2H), 5.41 (q, J = 8.1 Hz, 1H), 7.22-7.27 (m, 6H), 7.72-7.77 (m, 4H). ^{13}C NMR $CDCl_3$): 15.06, 18.40, 26.87, 27.05, 28.39, 37.29, 59.37, 114.21, 127.69, 129.72, 134.83, 135.04, 138.85. IR (neat): cm^{-1} 3080, 2940, 2860, 1960, 1890, 1820, 1590, 1430, 1390, 1115, 1080. Anal. Calcd for $C_{22}H_{28}OSi$: C, 78.52; H, 8.39. Found: C, 78.62; H, 8.24.

Hydrogen Peroxide Oxidation of 6: To a solution of **6** (269 mg, 0.80 mmol) in THF (2.0 mL) and methanol (2.0 mL), was added successively KF (334 mg, 5.8 mmol), $KHCO_3$ (360 mg, 3.2 mmol), and 30% H_2O_2 (0.35 mL, 3.6 mmol) at room temperature. The reaction mixture was stirred at room temperarure for 12 h. The mixture was subjected to the same workup and purification as above to give **7** in 67% yield.

3-[(Ethoxy)diphenylsilyl]-4-isopropylcyclohexene (10). Overall 72 % yield based on **8**. $R_f = 0.30$ (hexane/AcOEt = 60/1). ^1H NMR ($CDCl_3$): δ 0.82 (d, J = 6.7 Hz, 3H), 0.86 (d, J = 6.7 Hz, 3H), 1.17 (t, J = 7.0 Hz, 3H), 1.30-2.05 (m ,6H), 2.32-2.38 (m, 1H), 3.73 (q, J = 7.0 Hz, 2H), 5.57-5.80 (m, 2H), 7.35-7.40 (m, 6H), 7.58-7.68 (m, 4H). ^{13}C NMR ($CDCl_3$): δ -15.63, 18.33, 18.86, 21.87, 21.96, 22.33, 28.75, 29.10, 38.75, 59.52, 126.08, 126.21, 127.59, 127.71, 129.59, 129.64, 135.07, 135.23. IR (neat): cm^{-1} 3030, 2960, 2880, 1960, 1890, 1830, 1645, 1590, 1430, 1105, 1080, 950. Anal. Calcd for $C_{23}H_{30}OSi$: C, 78.80; H, 8.62. Found: C, 78.52; H, 8.68.

***trans*-6-Isopropyl-2-cyclohexen-1-ol (11).** (1) To a solution of **2** in THF (11.0 mL), which was prepared from **1** (7.58 mmol) and CuCN (7.58 mmol), was added a solution of **8** (0.32 g, 1.22 mmol) in THF (2.5 mL) over 18 min at 0 °C and the solution was stirred at 0 °C for 72 h. The reaction was quenched a 10% aq. solution of NH_4Cl and filtered to remove the resulting salts. The filtrate was extracted with Et_2O (12 mL x 3) and the combined organic layer was washed with water (10 mL x 2), dried over Na_2SO_4, and concentrated to give crude **9** (1.90 g). (2) To a solution of **9** in THF (8.0 mL) and MeOH (8.0 mL) was added successively $KHCO_3$ (3.10 g, 30.9 mmol), KF (3.20 g, 55.0 mmol), and 30% H_2O_2 (7.71 mL, 68.2 mmol) and the mixture was stirred for 96 h. To the mixture was added anhydrous $Na_2S_2O_3$ to the amount that the excess H_2O_2 was consumed completely. The mixture was filtered and concentrated. The residue was diluted with Et_2O (15 mL), washed with 1 M NaOH (10 mL x 3), water (10 mL), and dried over Na_2SO_4, and concentrated. The residue was subjected to column chromatography on silica gel (20 mL) eluted with hexane/AcOEt (15/1) to afford **11** (94 mg, overall 55% yield based on **8**) (R_f = 0.13). ^1H NMR ($CDCl_3$): δ 0.84 (d, J = 6.8 Hz, 3H), 0.96 (d, J = 6.8 Hz, 3H), 1.22-1.33 (m, 3H), 1.59-1.71 (m, 1H), 1.96-2.07 (m, 3H), 3.98-4.10 (m, 1H), 5.60-5.68 (m, 1H), 5.72-5.81 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 17.16, 20.69, 21.06, 25.31, 26.62, 48.01, 68.92, 129.58, 130.92. IR (neat): cm^{-1} 3332, 2968, 2880, 1658, 1468, 1388, 1192. Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.11; H, 11.70.

***trans*-3-Cyclohexene-1,2-diol (14).** (1) To a solution of **1** (4.08 mol) in THF (3.0 mL) was added **12** (204 mg, 2.12 mmol) at 0 °C and the reaction mixture was stirred for 2 h. The reaction was quenched with a 10% aq. solution of NH_4Cl (10 mL) and extracted with Et_2O (10 mL x 3). The combined organic layer was washed with water (10 mL x 2), dried over Na_2SO_4, and concentrated to give crude **13** (1.19 g). (2) To a solution of **13** in THF (3.0 mL) and MeOH (3.0 mL) was added successively $KHCO_3$ (860 mg, 8.61 mmol), KF (890 mg, 15.3 mmol), and 30% H_2O_2 (1.08mL, 9.56 mmol) and the mixture was stirred for 12 h. To the mixture was added anhydrous $Na_2S_2O_3$ to the amount that the excess H_2O_2 was

consumed completely. The mixture was dried over Na_2SO_4, and concentrated. The residue was subjected to column chromatography on silica gel (35 mL) eluted with hexane/AcOEt (1/2) to afford **11** (180 mg, overall 51% yield based on **8**) (R_f = 0.30) as colorless crystal. Recrystallization was performed from hexane-AcOEt. mp 75.9-76.7 °C. ^{1}H NMR (DMSO-d_6, δ 2.50 ppm):[17] δ 1.37-1.52 (m, 1H), 1.68-1.77 (m, 1H), 1.96-2.01 (m, 2H), 3.33-3.42 (m, 1H), 3.71-3.74 (m, 1H), 4.66 (d, J = 4.0 Hz, 1H), 4.76 (d, J = 5.3 Hz, 1H), 5.46 (dq, J = 10.2 and 2.2 Hz, 1H), 5.43-5.62 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 24.78, 28.46, 73.57, 128.07, 129.14. IR (KBr): cm^{-1} 3330, 3270, 3045, 2920, 1090, 1060. Anal. Calcd for $C_6H_{10}O_2$: C, 63.13; H, 8.83. Found: C, 62.86; H, 8.55.

***trans*-2-Cyclohexene-1,4-diol (16).** To a solution of **2** in THF (5.5 mL), which was prepared from **1** (2.18 mmol) and CuCN (2.20 mmol), was added a solution of **12** (140 mg, 1.08 mmol) in THF (1.0 mL) at -78 °C. The reaction mixture was stirred at -78 °C for 2 h and warmed to the ambient temperature. The reaction was quenched with 10% aq. solution of NH_4Cl (16 mL) and filtered. The filtrate was extracted with Et_2O (10 mL x 3), washed with water (10 mL x 2), dried over Na_2SO_4, and concentrated. The residue was subjected to column chromatography on silica gel (24 mL) eluted with hexane/AcOEt (1/2) to afford a mixture of **16** and **14** (102 mg, **16/14** = 92/8 determined by means of ^{1}H NMR) (R_f = 0.13) as colorless crystal in overall 83% yield based on **12**. Pure **16** was obtained by recrystallization from hexane-AcOEt. mp 85.9-86.9 °C. ^{1}H NMR (DMSO-d_6, δ 2.50 ppm):[17] δ 1.25-1.34 (m, 2H), 1.86-1.93 (m, 2H), 3.95-4.05 (m, 2H), 4.70 (d, J = 5.3 Hz, 2H), 5.57 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 30.40, 66.23, 132.66. IR (KBr): cm^{-1} 3325, 2950, 2875, 1450, 1390, 1300, 1060, 955. Anal. Calcd for $C_6H_{10}O_2$: C, 63.13; H, 8.83. Found: C, 62.78; H, 8.53.

1-[(Ethoxy)diphenylsilyl]-2-propenyl-1-octene (19). Overall 56% yield based on **17**. R_f = 0.18 (hexane/AcOEt = 40/1). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, J = 6.7 Hz, 3H), 1.20 (t, J = 7.0 Hz, 3H), 1.22-1.38 (m, 6H), 1.40-1.55 (m, 2H), 2.16 (t, J = 7.2 Hz, 2H), 2.89 (dt, J = 6.9 and 1.3 Hz, 2H), 3.77 (q, J = 7.0

Hz, 2H), 4.78-4.89 (m, 2H), 5.41-5.62 (m, 1H), 5.65 (s, 1H), 7.34-7.39 (m, 6H), 7.61-7.65 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 14.09, 18.33, 22.65, 27.86, 29.03, 31.75, 38.69, 41.20, 59.18, 116.20, 117.83, 127.74, 129.57, 134.79, 136.00, 136.28, 163.24. IR (neat): cm^{-1} 3025, 2940, 2900, 2830, 1950, 1880, 1810, 1595, 1415, 1100, 1065. Anal. Calcd for $C_{25}H_{34}OSi$: C, 79.31; H, 9.05. Found: C, 79.41; H, 9.01.

Preparation of [(Diethylamino)diphenylsilyl](methyl)magnesium (3) and Synthesis of 2-Propenyl-octanal (20).[19] (1) To a solution of **1** (4.22 mmol) in THF (3.5 mL) was added MeMgBr in Et_2O (1.50 mL, 4.25 mmol) at 0 °C and the solution was stirred at 0 °C for 1 h to give a solution of **3**. To the solution was added CuI (403 mg, 2.12 mmol) in one portion at 0 °C and the stirring was continued for 1 h. To the solution was added a solution of **17** (200 mg, 1.86 mmol) in THF (1.0 mL) over 2 min at 0 °C and the reaction mixture was stirred at 0 °C for 3 h. To the mixture was added allyl bromide (0.440 mL, 5.08 mmol) at 0 °C. The mixture was warmed to the ambient temperature slowly. The reaction mixture was decomposed with 5% aq. solution of NH_4Cl (10 mL) and filtered. The filtrate was extracted with Et_2O (10 mL x 4), washed with water (10 mL x 2), dried over Na_2SO_4, and concentrated to give crude **18**. (2) To a solution of **18** in THF (4.0 mL) and MeOH (4.0 mL) was added successively $KHCO_3$ (1.69 g, 16.9 mmol), KF (1.73 g, 30.9 mmol), and 30% H_2O_2 (6.45 mL, 57.1 mmol) and the reaction mixture was stirred at room temperature for 64 h. Water (12 mL) was poured into the mixture, which was extracted with Et_2O (12 mL x 4). The combined organic layer was washed with 10% aq. solution of $Na_2S_2O_3$ (15 mL), saturated aqueous solution of $NaHCO_3$ (15 mL), water (15 mL), dried over Na_2SO_4, and concentrated. The residue was subjected to column chromatography on silica gel (50 mL) eluted with hexane/AcOEt (30/1) (R_f = 0.33) and subsequent MPLC eluted with hexane/AcOEt (40/1) to give **20** (111 mg, overall 36% yield based on **17**) as colorless oil. ^1H NMR ($CDCl_3$): δ 0.83-0.90 (m, 3H), 1.20-1.35 (m, 8H), 1.42-1.72 (m, 1H), 2.13-2.45 (m, 3H), 5.02-5.10 (m, 2H), 5.63-5.83 (m, 1H), 9.60 (d, J = 2.3 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 14.04, 22.56, 26.87, 28.39, 29.31,

31.60, 33.05, 51.28, 117.08, 135.02, 204.94. IR (neat): cm^{-1} 2936, 2864, 2724, 1732, 1646, 1468, 994, 916.

Ethyl *anti*-3-[(diethylamino)diphenylsilyl]-2-methylbutanoate (22). To a solution of **1** (2.05 mmol) in THF (4.0 mL) was added HMPA (0.357 mL, 2.05 mmol) at 0 °C and the mixture was cooled to -78 °C. Ethyl crotonate **21** (0.255 mL, 2.05 mmol) was added dropwise. After being stirred for 1 h, the reaction was quenched with methyl iodide (0.256 mL, 4.11 mmol) and stirred for another 1 h. The mixture was allowed to warm to the ambient temperature. The mixture was poured into a 10% aq. solution of NH_4Cl (30 mL) and extracted with Et_2O (30 mL x 3). The combined organic layer was washed with a 10% aq. solution of NH_4Cl (10 mL x 1), dried over Na_2SO_4, and concentrated to give crude **22**. The pure sample was obtained by preparative GLC. The product was used in the next step without further purification. ^1H NMR (C_6D_6): δ 0.94 (t, J = 7.0 Hz, 6H), 1.00 (t, J = 7.1 Hz, 3H), 1.05 (d, J = 7.1 Hz, 3H), 1.27 (d, J = 7.6 Hz, 3H), 2.49 (dq, J = 7.6 and 2.9 Hz, 1H), 2.98 (q, J = 7.0 Hz, 4H), 3.11 (dq, J = 7.1 and 2.9 Hz, 1H), 3.99 (q, J = 7.1 Hz, 1H), 4.00 (q, J = 7.1 Hz, 1H), 7.22-7.30 (m, 6H), 7.71-7.82 (m, 4H).

Ethyl *anti*-3-[(ethoxy)diphenylsilyl]-2-methylbutanoate (23). To the product obtained above and NH_4Cl (59 mg, 1,1 mmol) was added ethanol (10 mL) and the reaction mixture was stirred for 24 h. After concentrated, the residue was diluted with hexane (20 mL) and filtered. The filtrate was concentrated in vacuo. The remaining oil was subjected to column chromatography on silica gel eluted with hexane/AcOEt (20/1, R_f = 0.15) to give **23** (500 mg, 78%) as a single stereoisomer.[20] ^1H NMR (C_6D_6): δ 1.00 (t, J = 7.0 Hz, 3H), 1.10 (t, J = 7.0 Hz, 3H), 1.22 (d, J = 7.0 Hz, 3H), 1.23 (d, J = 7.6 Hz, 3H), 2.36 (dq, J = 7.6 and 4.7 Hz, 1H), 3.01 (dq, J = 7.0 and 4.7 Hz, 1H), 3.66 (q, J = 7.0 Hz, 2H), 3.97 (q, J = 7.0, 1H), 3.99 (q, J = 7.0, 1H), 7.25-7.27 (m, 6H), 7.70-7.78 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 9.74, 13.46, 14.22, 18.26, 21.33, 39.03, 59.53, 60.09, 127.76, 127.84, 129.78, 129.87, 133.82, 133.91, 135.11, 135.22. IR (neat): cm^{-1} 3080,

2980, 2880, 1960, 1890, 1830, 1735, 1590, 1190, 1110, 1080, 950. Anal. Calcd for $C_{21}H_{28}O_3Si$: C, 70.74; H, 7.92. Found: C, 70.47; H, 7.98.

Ethyl *anti*-3-hydroxy-2-methylbutanoate (24). To a solution of **23** (264 mg, 0.740 mmol) in THF (3.0 mL) and ethanol (1.0 mL) were added successively KF (310 mg, 5.33 mmol), $KHCO_3$, (300 mg, 2.96 mmol), and 30% H_2O_2 (0.328 mL, 3.33 mmol) at room temperature. The reaction mixture was stirred for 12 h at room temperature. The mixture was worked up in an usual manner. The residual oil was subjected to column chromatography on silica gel eluted with hexane/AcOEt (3/1, R_f = 0.20) gave **24** (37 mg, 35% yield) as a single stereoisomer. ^1H NMR (C_6D_6): δ 0.95 (t, J = 7.2 Hz, 3H), 1.07 (d, J = 3.8 Hz, 3H), 1.08 (d, J = 4.6 Hz, 3H), 2.33 (dq, J = 7.1 and 7.0 Hz, 1H), 2.43 (m, 1H), 3.80 (m, 1H), 3.94 (q, J = 7.2 Hz, 2H). IR (neat): cm^{-1} 3450, 1740, 1190, 1120. Anal. Calcd for $C_7H_{14}O_3$: C, 57.51; H, 9.65. Found: C, 57.33; H, 9.51.

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Chapter 5

Electronic Spectra of (Amino)(phenyl)disilanes

Abstract: UV absorption spectra of a series of (amino)(phenyl)disilanes have been interpreted in terms of the n - σ conjugation between the nonbonding electrons on nitrogens and the Si-Si σ-bonding electrons which are activated by the σ - π conjugation with the phenyl groups. X-ray crystal structure of a 1,1,2,2-tetraamino-1,2-diphenyldisilane has also been determined.

Introduction

Polysilanes have been extensively studied because of their unique electronic properties due to the so-called σ-conjugation.[1] The Ph-Si-Si system also has an interesting electronic properties that the Si-Si bond conjugates with the phenyl group: The conjugating properties has been rationalized at first in terms of d - π* interaction in the excited state, and later, in addition to this, in terms of σ - π interaction in the ground state.[2-5] This σ - π interaction raises the HOMO level of the Ph-Si-Si system ($\sigma_{Si\text{-}Si} + \pi$), the first ionization energy (IE) being estimated to be 8.35 eV.[6]

Functionalized oligo- and polysilanes,[7] however, have little been examined in terms of the electronic structure. Only a few reports have reported UV spectra of heteroatom(X)-substituted permethylated oligosilanes including aminodisilanes.[8-9] The spectra were interpreted in terms of p_x - $\sigma_{Si\text{-}Si}$ (n - σ) and p_x - d_{Si} (pπ - dπ) interactions.

If a functional group, such as an amino group, is attached to the Ph-Si-Si system, a p_N orbital of the amino group (IE 8.06 eV)[10] is expected to interact with the activated HOMO orbital ($\sigma_{Si\text{-}Si} + \pi$) of the Ph-Si-Si system (IE 8.35 eV) to give a noble electronic structure, as shown in Figure 1. However, the functionalized Ph-Si-Si system has little been studied so far in terms of the electronic structure because of a difficulty in the synthesis of such compounds.[11] The author has found a systematic method for the preparation of (amino)(phenyl)disilanes, which involves

coupling of (amino)(phenyl)silyllithums with appropriate (amino)chlorosilanes[12] In this chapter, the author described study of the electronic spectra of the (amino)(phenyl)disilanes in order to clarify the electronic effect of amino groups on the Ph-Si-Si system.

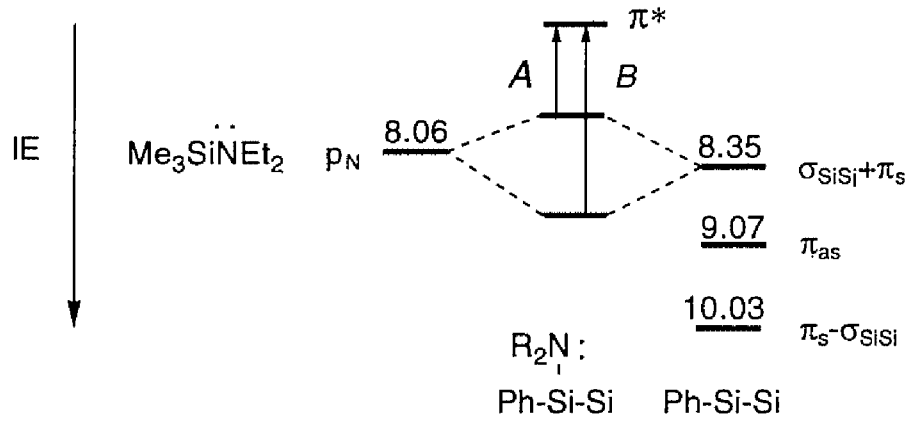


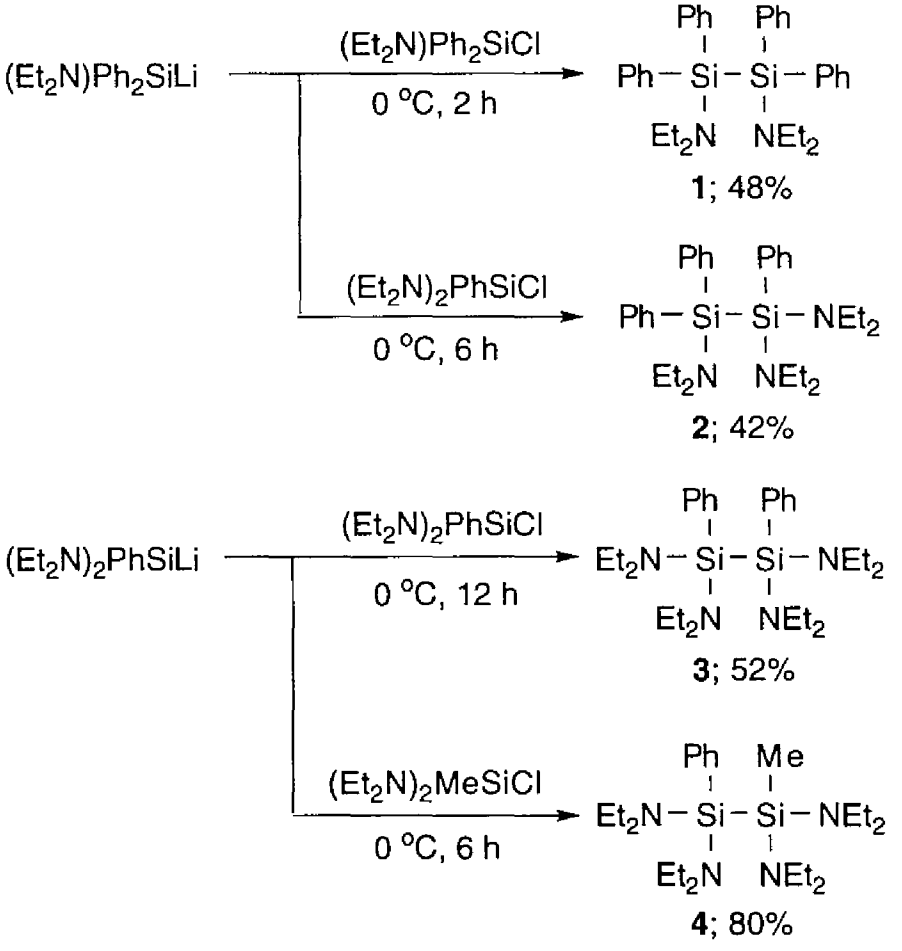
Figure 1. A qualitative MO model for the origin of two absorptions of (amino)(phenyl)disilanes

Results and Discussion

1. Synthesis of (Amino)(phenyl)disilanes

1,2-(Diamino)tetraphenyl- (**1**), 1,1,2-(triamino)triphenyl- (**2**), 1,1,2,2-(tetraamino)diphenyl- (**3**), and 1,1,2,2-(tetraamino)-methylphenyldisilane (**4**) were prepared by coupling between appropriate (amino)silyllithiums and (amino)chlorosilanes, as shown in Scheme 1.

Scheme 1



2. UV Spectra

Table 1 summarizes absorption maxima for **1** - **4**, together with data for 1,1,2,2-(tetraamino)-1,2-dimethyldisilane (**5**) and 1,2-dimethyl-1,1,2,2-tetraphenyldisilane (**6**) for reference. Some selected spectra are shown in Figure 2.

All the (amino)(phenyl)disilanes exhibit two absorption maxima: a strong band around 220 nm and a weak band around 280 nm. They are different from those of (amino)(methyl)disilanes (**5**) which shows only one weak absorption at 238 nm and

of phenylmethyldisilane (**6**) which exhibits a strong absorption around 240 nm and weak around 270 nm characteristic of a typical Ph-Si-Si system. No solvent effect is observed for **3** upon changing the solvent from cyclohexane to acetonitrile (Table 1).

The two absorptions observed for (amino)(phenyl)disilanes are well compatible with expectation (Figure 1). Thus, the energetically favorable interaction between p_N orbital ($\Psi(N)$) and $\sigma_{Si-Si} + \pi$ orbital ($\Psi(Si)$), i.e., n - σ conjugation, will form two energy levels which lead to two electronic transitions *A* and *B*. Judging from the energy levels, the HOMO is primarily of p_N character. Since a transition from the p_N orbital to π^* is locally forbidden, the transition from the HOMO will be forbidden to the extent that $\Psi(N)$ contributes to the wave function. The weak band around 280 nm can thus be ascribed to a locally forbidden transition from the HOMO (*A* in Figure 1). Since an increase in the number of amino groups results in more effective n - σ conjugation making the HOMO higher in energy, red shifts of the 280 nm absorptions are observed in the order of **1**, **2**, and **3** with some reduction in the intensity. The insensitivity of the band to the solvent polarity, as observed for **3**, shows the electron density of p_N to be delocalized through n - σ^* or $p\pi$ - $d\pi$ conjugation. This insensitivity of the UV absorption of aminosilanes has been reported previously.[8] The bands are broad since they are overlapped by bands arising from transitions associated with the phenyl groups .

The absorption around 220 nm can be ascribed to a transition from the next HOMO (*B* in Figure 1). This transition may thus be regarded as a blue shift of transition from $\sigma_{Si-Si} + \pi$ to π^* in the Ph-Si-Si system.

Table 1. Absorption Maxima of Some Disilanes in Cyclohexane

disilane		λ_{max} nm (ε)	
$(Et_2N)Ph_2SiSiPh_2(NEt_2)$	(1)	227 (27900)	274 (6050)
$(Et_2N)Ph_2SiSiPh(NEt_2)_2$	(2)	222 (30400)	277 (5090) sh
$(Et_2N)_2PhSiSiPh(NEt_2)_2$	(3)	220 (27100)	285 (3600)
		217 (25000)[a]	285 (3120)[a]
$(Et_2N)_2PhSiSiMe(NEt_2)_2$	(4)	218 (17000)	277 (1690) sh
$(Et_2N)_2MeSiSiMe(NEt_2)_2$	(5)	<210	238 (7560) sh
$MePh_2SiSiPh_2Me$	(6)	239 (26900)	268 (3560) sh
			273 (2310) sh

[a] In acetonitrile

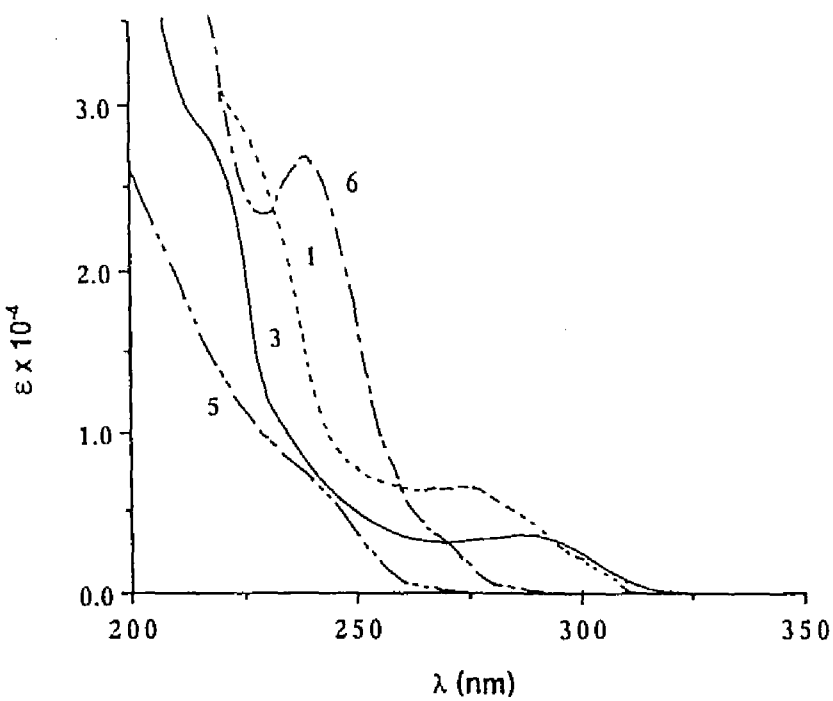


Figure 2. UV spectra of 1, 3, 5, and 6 in cyclohexane.

To get a further insight into the n - σ conjugation, the author determined the X-ray crystal structure of **3**. The structure is shown in Figure 3 and selected bond lengths and angles are listed in Table 2.

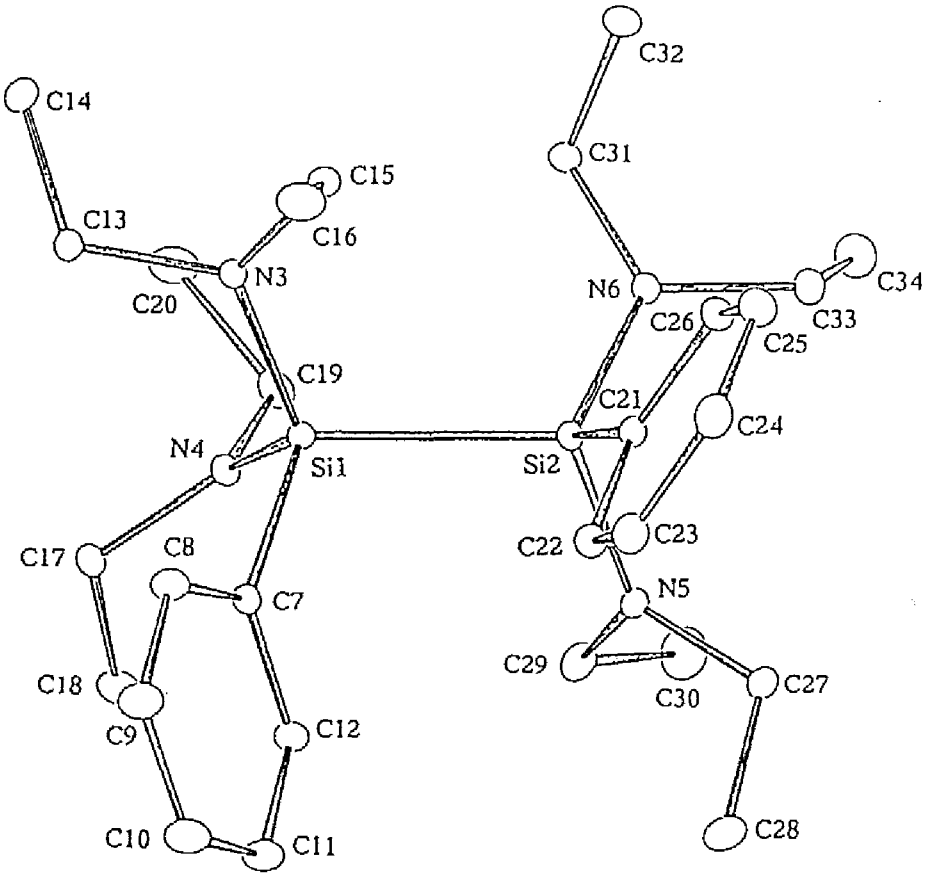


Figure 3. Crystal structure of 3. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å), Angles (degree) and Dihedral Angles (degree) for **3**

	Bond Distances		
Si(1)-N(3)	1.727 (1)	Si(1)-N(4)	1.724 (2)
Si(2)-N(5)	1.724 (1)	Si(2)-N(6)	1.729 (2)
Si(1)-Si(2)	2.391 (6)		
	Bond Angles		
N(3)-Si(1)-Si(2)	110.02 (6)	N(4)-Si(1)-Si(2)	112.88 (5)
N(5)-Si(2)-Si(1)	108.76 (6)	N(6)-Si(2)-Si(1)	113.35 (6)
	Dihedral Angles		
Si(1)Si(2)N(3) - C(13)N(3)C(15)	17.31		
Si(1)Si(2)N(4) - C(17)N(4)C(19)	45.01		
Si(1)Si(2)N(5) - C(27)N(5)C(29)	43.38		
Si(1)Si(2)N(6) - C(31)N(6)C(33)	13.38		

Geometry around all nitrogen atoms is nearly planar as generally observed [13,14] (sum of three angles around nitrogen: N(3), 357.9°; N(4), 359.3°; N(5), 359.3°; N(6), 359.7°). The p_N orbital on nitrogen is thus assumed to be perpendicular to the plane. The dihedral angle (θ) between two planes defined by the Si-Si-N and C-N-C fragments implies the degree of interaction between the p_N orbitals and the σ_{Si-Si} orbital (n - σ conjugation): θ=90° makes these orbitals parallel, resulting in the strongest interaction. The observed angles θ's are as follows: N(3), 17°; N(4), 45°; N(5), 43°; N(6), 13°. The data suggest that the p_N orbitals on N(4) and N(5) have higher possibility to interact with the σ_{Si-Si} orbital than those on N(3) and N(6). However, all Si-N bond distances are normal, having an average value 1.73Å. The Si-Si bond length 2.391Å is slightly longer than the normal range (2.33 - 2.37Å).[14] There is thus no structural bias which might be anticipated by the n - σ conjugation.

The author next examined UV spectra of **3** in solid state, the spectrum being shown in Figure 4. The observed absorptions are not significantly different from those observed in solution (Figure 2). The author could not obtained evidence for the angle-dependence of the n - σ conjugation. The high planarity of all the four nitrogen atoms might rather imply the angle-independence of the n - σ conjugation.

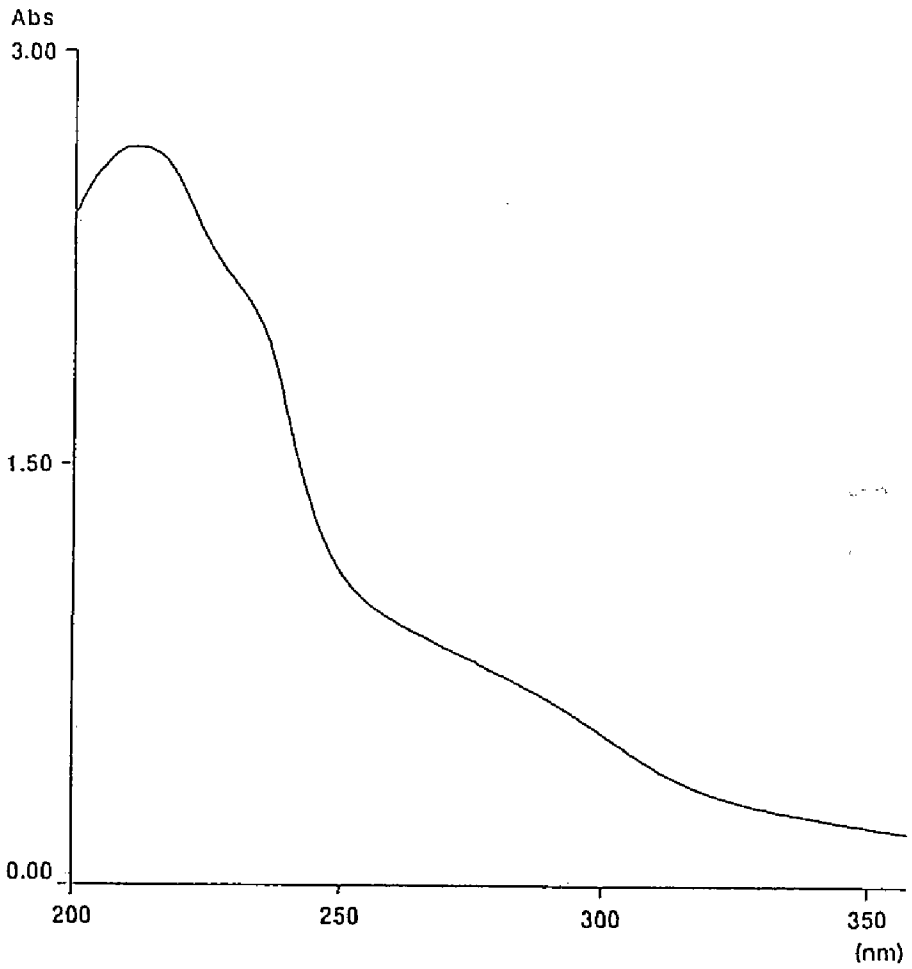


Figure 4. UV spectra of 3 in solid state (KBr pellet)

Table 3. Crystal Data and Experimental Details for Structure Determination of **3**

chemical formula	$C_{28}H_{50}Si_2N_4$
formula weight	498.90
crystal size, mm	0.30 x 0.40 x 0.35
crystal system	monoclinic
space group	$P2_1/a$
unit-cell dimensions	
a, Å	18.900 (4)
b, Å	10.365 (3)
c, Å	16.254 (4)
β, degrees	104.33 (2)
V, Å^3	3085 (1)
Z	4
ρ_{calcd}, gcm^{-3}	1.07
temp, °C	25
radiation	Cu K_α (λ = 1.54178 Å)
μ(Cu K_α), cm^{-1}	11.07
No. of unique reflections	5094
No. of reflections used	4786
No. of variables	467
R	0.042
Rw	0.051
S	2.36

Table 4. Atomic Coordinates and Equivalent Isotropic Thermal Parameters with Estimated Standard Deviations in Parentheses for **3**

atom	X	Y	Z	B (eq)
Si 1	0.05891 (2)	-0.24847 (5)	-0.23899 (3)	3.46 (2)
Si 2	0.18390 (2)	-0.26119 (5)	-0.24475 (3)	3.43 (2)
N 3	0.00460 (8)	-0.3337 (2)	-0.32234 (9)	4.08 (5)
N 4	0.04575 (8)	-0.2938 (2)	-0.14182 (9)	4.05 (4)
N 5	0.23570 (8)	-0.1669 (2)	-0.16481 (9)	4.04 (4)
N 6	0.21637 (8)	-0.4176 (1)	-0.2412 (1)	4.19 (4)
C 7	0.03596 (9)	-0.0710 (2)	-0.2479 (1)	3.90 (5)
C 8	-0.0150 (1)	-0.0201 (2)	-0.3170 (1)	5.21 (6)
C 9	-0.0268 (2)	0.1114 (2)	-0.3264 (2)	6.72 (8)

(continued)

Table 4. (continued)

C 10	0.0118 (2)	0.1954 (2)	-0.2673 (2)	7.00 (9)
C 11	0.0624 (1)	0.1483 (2)	-0.1977 (2)	6.14 (8)
C 12	0.0738 (1)	0.0172 (2)	-0.1885 (1)	4.77 (6)
C 13	-0.0744 (1)	-0.3452 (2)	-0.3304 (2)	5.14 (6)
C 14	-0.1056 (1)	-0.4775 (3)	-0.3540 (2)	6.60 (9)
C 15	0.0279 (1)	-0.3674 (2)	-0.3995 (1)	4.87 (6)
C 16	0.0013 (2)	-0.2790 (3)	-0.4746 (2)	7.6 (1)
C 17	-0.0049 (1)	-0.2310 (2)	-0.0995 (1)	4.92 (6)
C 18	0.0307 (2)	-0.1777 (3)	-0.0127 (2)	7.3 (1)
C 19	0.0762 (1)	-0.4139 (2)	-0.1009 (2)	5.75 (7)
C 20	0.0230 (2)	-0.5236 (3)	-0.1114 (2)	8.6 (1)
C 21	0.19114 (9)	-0.1798 (2)	-0.3466 (1)	3.80 (5)
C 22	0.1701 (1)	-0.0518 (2)	-0.3646 (1)	4.73 (6)
C 23	0.1720 (1)	0.0054 (2)	-0.4411 (2)	5.84 (7)
C 24	0.1948 (1)	-0.0641 (3)	-0.5017 (2)	6.16 (8)
C 25	0.2158 (1)	-0.1900 (3)	-0.4863 (1)	6.18 (8)
C 26	0.2137 (1)	-0.2476 (2)	-0.4099 (1)	4.89 (6)
C 27	0.2958 (1)	-0.0836 (2)	-0.1747 (2)	4.98 (6)
C 28	0.2862 (2)	0.0583 (3)	-0.1580 (2)	7.8 (1)
C 29	0.2303 (1)	-0.1791 (3)	-0.0769 (1)	6.02 (8)
C 30	0.2923 (2)	-0.2475 (4)	-0.0176 (2)	9.4 (1)
C 31	0.1717 (1)	-0.5344 (2)	-0.2565 (2)	4.94 (6)
C 32	0.1781 (2)	-0.6127 (3)	-0.3334 (2)	6.99 (9)
C 33	0.2950 (1)	-0.4384 (2)	-0.2315 (2)	5.53 (7)
C 34	0.3306 (2)	-0.5329 (3)	-0.1629 (2)	8.0 (1)
H 8	-0.040 (1)	0.077 (2)	-0.357 (2)	6.78 (0)
H 9	-0.064 (2)	0.143 (3)	-0.376 (2)	6.78 (0)
H 10	0.006 (2)	0.291 (3)	-0.275 (2)	6.99 (0)
H 11	0.088 (2)	0.202 (3)	-0.157 (2)	6.12 (0)
H 12	0.112 (1)	-0.013 (2)	-0.141 (2)	4.72 (0)
H 13A	-0.104 (1)	-0.279 (2)	-0.373 (2)	5.08 (0)
H 13B	-0.082 (1)	-0.317 (2)	-0.273 (2)	5.08 (0)
H 14A	-0.160 (2)	-0.484 (3)	-0.358 (2)	6.49 (0)
H 14B	-0.099 (2)	-0.508 (3)	-0.407 (2)	6.49 (0)
H 14C	-0.083 (2)	-0.538 (3)	-0.313 (2)	6.49 (0)
H 15A	0.014 (1)	-0.459 (2)	-0.415 (2)	4.77 (0)
H 15B	0.084 (1)	-0.367 (2)	-0.383 (1)	4.77 (0)
H 16A	0.012 (2)	-0.191 (3)	-0.462 (2)	7.46 (0)

(continued)

Table 4. (continued)

H 16B	-0.054 (2)	-0.266 (3)	-0.462 (2)	7.46 (0)
H 16C	0.016 (2)	-0.311 (3)	-0.522(2)	7.46 (0)
H 17A	-0.046 (1)	-0.295 (2)	-0.098 (1)	4.72 (0)
H 17B	-0.031 (1)	-0.162 (2)	-0.138 (2)	4.72 (0)
H 18A	0.057 (2)	-0.242 (3)	0.020 (2)	7.00 (0)
H 18B	-0.005 (2)	-0.140 (3)	0.010 (2)	7.00 (0)
H 18C	0.068 (2)	-0.107 (3)	-0.019 (2)	7.00 (0)
H 19A	0.120 (1)	-0.442 (2)	-0.123 (2)	5.51 (0)
H 19B	0.100 (1)	-0.412 (2)	-0.037 (2)	5.51 (0)
H 20A	0.052 (2)	-0.602 (3)	-0.078 (2)	8.26 (0)
H 20B	0.012 (2)	-0.539 (3)	-0.172 (2)	8.26 (0)
H 20C	-0.019 (2)	-0.499 (3)	-0.088 (2)	8.26 (0)
H 22	0.151 (1)	-0.001 (2)	-0.322 (1)	4.60 (0)
H 23	0.157 (1)	0.092 (3)	-0.450 (2)	5.71 (0)
H 24	0.193 (1)	-0.026 (3)	-0.558 (2)	6.03 (0)
H 25	0.230 (1)	-0.245 (3)	-0.529 (2)	5.95 (0)
H 26	0.227 (1)	-0.334 (2)	-0.402 (2)	4.72 (0)
H 27A	0.301 (1)	-0.098 (2)	-0.236 (2)	4.90 (0)
H 27B	0.342 (1)	-0.113 (2)	-0.134 (2)	4.90 (0)
H 28A	0.329 (2)	0.101 (3)	-0.161 (2)	7.70 (0)
H 28B	0.237 (2)	0.091 (3)	-0.197 (2)	7.70 (0)
H 28C	0.278 (2)	0.068 (3)	-0.100 (2)	7.70 (0)
H 29A	0.183 (2)	-0.222 (3)	-0.076 (2)	5.97 (0)
H 29B	0.235 (1)	-0.099 (3)	-0.034 (2)	5.97 (0)
H 30A	0.284 (2)	-0.246 (3)	0.043 (2)	9.38 (0)
H 30B	0.338 (2)	-0.208 (4)	-0.016 (2)	9.38 (0)
H 30C	0.277 (2)	-0.329 (4)	-0.051 (2)	9.38 (0)
H 31A	0.120 (1)	-0.507 (2)	-0.264 (1)	4.76 (0)
H 31B	0.185 (1)	-0.590 (2)	-0.202 (2)	4.76 (0)
H 32A	0.146 (2)	-0.680 (3)	-0.341 (2)	6.78 (0)
H 32B	0.227 (2)	-0.645 (3)	-0.326 (2)	6.78 (0)
H 32C	0.166 (2)	-0.562 (3)	-0.388 (2)	6.78 (0)
H 33A	0.320 (1)	-0.354 (3)	-0.218 (2)	5.42 (0)
H 33B	0.306 (1)	-0.473 (2)	-0.287 (2)	5.42 (0)
H 34A	0.386 (2)	-0.537 (3)	-0.157 (2)	7.98 (0)
H 34B	0.305 (2)	-0.619 (3)	-0.176 (2)	7.98 (0)
H 34C	0.319 (2)	-0.513 (3)	-0.112 (2)	7.98 (0)

Experimental Section.

General Remarks. ^{1}H (200 MHz), ^{13}C (50.29 MHz), ^{29}Si (39.73 MHz) NMR spectra were recorded on a Varian VXR-200 spectrometer. ^{1}H and ^{13}C chemical shifts are referenced to internal benzene-d_6 (^{1}H δ 7.200 ppm and ^{13}C δ 128.00 ppm). ^{29}Si chemical shifts are referenced to external Me_4Si (0 ppm). Mass spectra were recorded on a JEOL JMS-D300 mass spectrometer. UV spectra in solution were measured with a Hitachi U-3410 spectrometer. UV spectra in solid state (KBr pellet) were measured with a JASCO UVIDEC-610B spectrometer. Infrared spectra were recorded with a Hitachi 270-30 spectrometer. Melting points were measured with a Yanaco-MP-S3 apparatus. The elemental analyses were performed at the Microanalysis Center of Kyoto University: Analytical samples were purified by recrystallization or preparative GLC. Lithium granular was purchased from Chemetall Gesellshaft. Lithium dispersion (25 wt. % in mineral oil) was purchased from Aldrich. THF was distilled under nitrogen from sodium/benzophenone. Hexane and cyclohexane were distilled under nitrogen from sodium. Dichloromethane and acetnitrile were distilled under nitrogen from calcium hydride. All reactions were carried out under a nitrogen atmosphere. 1,1,2,2-Tetrakis(diethylamino)-1,2-dimethyldisilane (**5**) was prepared as described in the literature.[12b]

Preparation of (Amino)chlorosilanes: A Typical Procedure.

A solution of diethylamine (11.7 mL, 110 mmol) in dry THF (10 mL) was added to a mixture of triethylamine (15.5 mL, 110 mmol) and dichlorodiphenylsilane (20.7 mL, 100 mmol) in dry THF (150 mmol) at room temperature over 30 min with stirring. During the addition, a large amount of white salt (Et_3N•HCl) precipitated. After the addition was complete, the mixture was stirred at room temperature for 6 h. The mixture was diluted with hexane (100 mL) and then filtered. The filtrate was concentrated under reduced pressure. The residue was distilled under reduced pressure to give 24.9 g (86% yield) of (diethylamino)diphenylchlorosilane as a

viscous, colorless to pale yellow oil, bp 129-133 °C/0.55 mmHg (see also Chapter 1).

Preparation of (Amino)phenylsilyllithiums.[12a]

To a suspension of lithium dispersion (13 mg-atom; commercial 25 wt % in mineral oil was washed with dry hexane three times) in dry THF (4.0 mL) was added dropwise bis(diethylamino)phenylchlorosilane (815 mg, 2.86 mmol) at room temperature with stirring. After a few minutes, the resulting greenish mixture was stirred at 0 °C for 4 h to give a solution of bis(diethylamino)phenylsilyllithium. The solution was used in the next reaction without titration on the assumption of the quantitative yield.[12a] (Diethylamino)diphenylsilyllithum was prepared similarly from (diethylamino)diphenylchlorosilane and lithium granular in quantitative yield (see also Chapter 1).[12a]

A typical procedure: 1,1,2,2-Tetrakis(diethylamino)-1,2-diphenyldisilane (3).

A solution of bis(diethylamino)phenylsilyllithium in THF (4.0 ml; 2.86 mmol), prepared above, was separated from the excess lithium metal by transferring via syringe to another flask. To the solution was added bis(diethylamino)chlorosilane (785 mg, 2.70 mmol) over 5 min at 0 °C and then the solution was stirred at 0 °C for 12 h. After being warmed to room temperature, the solvent was evaporated under reduced pressure. The residue was diluted with dry hexane and filtered. The filtrate was evaporated. The resulting white solid was recrystallized from dichloromethane to give the disilane **3** (700 mg, 52% yield) as white crystals. mp 145 °C dec. ^{1}H NMR (C_6D_6): δ 1.06 (t, J = 7.0 Hz, 24H), 3.15 (q, J = 7.0 Hz, 16H), 7.27-7.31 (m, 6H), 7.77-7.82 (m, 4H). ^{13}C NMR (C_6D_6): δ 14.29, 39.74, 127.62, 128.93, 135.75, 141.89. ^{29}Si NMR (C_6D_6): δ -16.31. MS: m/e 498 (M^+, 1), 249 ($(Et_2N)_2PhSi^+$, 100). IR (KBr): 2972, 2940, 2856, 1380, 1202, 1170, 1098, 1020, 926, 704, 490 cm^{-1}. Anal. Calcd for $C_{28}H_{50}N_4Si_2$: C, 67.41, H, 10.10. Found: C, 67.40, H, 10.01.

1,2-Bis(diethylamino)-1,1,2,2-tetraphenyldisilane (1).

This compound was obtained similarly as white crystals (recrystallization from dichloromethane) in 48% yield. mp 149-150.5 °C. ^{1}H NMR (C_6D_6): δ 0.96 (t, J = 7.0 Hz, 12H), 3.14 (q, J = 7.0 Hz, 8H), 7.20-7.24 (m, 12H), 7.71-7.76 (m, 8H). ^{13}C NMR (C_6D_6): δ 14.77, 41.69, 128.00, 129.39, 136.23, 139.02. ^{29}Si NMR (C_6D_6): δ -14.30. MS: m/e 508 (M^+, 28), 436 (M^+-Et_2N, 39), 254 ($(Et_2N)Ph_2Si^+$, 100). IR (KBr): 2972, 2936, 2860, 1430, 1376, 1202, 1170, 1100, 1022, 736, 702, 498 cm^{-1}. Anal. Calcd for $C_{32}H_{40}N_2Si_2$: C, 75.53, H, 7.92. Found: C, 75.58, H, 8.00.

1,1,2-Tris(diethylamino)-1,2,2-triphenyldisilane (2).

This compound was obtained similarly as white crystals (recrystallization from benzene) in 42%. mp 155-158 °C. ^{1}H NMR (C_6D_6): δ 0.96-1.05 (m, 18H), 3.07-3.19 (m, 12H), 7.23-7.28 (m, 6H), 7.71-7.81 (m, 9H). ^{13}C NMR (C_6D_6): δ 14.30, 14.69, 39.93, 41.48, 127.54, 127.85, 129.13, 129.17, 135.78, 136.17, 139.95, 141.02. ^{29}Si NMR (C_6D_6): δ -14.84, 15.95. MS: m/e 503 (M^+,.6), 254 ($(Et_2N)Ph_2Si^+$,.5), 249 ($(Et_2N)_2PhSi^+$, 100). IR (KBr): 2976, 2936, 2856, 1430, 1380, 1204, 1170, 1098, 1022, 928, 738, 702, 494 cm^{-1}. Anal. Calcd for $C_{30}H_{45}N_3Si_2$: C, 71.51, H, 9.00. Found: C, 71.32, H, 9.03.

1,1,2,2-Tetrakis(diethylamino)-1-methyl-2-phenyldisilane (4).

This compound was prepared similarly and isolated by bulb-to-bulb distillation in 80% yield as white solids. bp 225-245 °C/1.30 mmHg (bath temperature). mp 123.5-125 °C. ^{1}H NMR (C_6D_6): δ 0.41 (s, 3H), 1.03 (t, J = 7.0 Hz, 12H), 1.13 (t, J = 7.0 Hz, 12H), 2.99 (q, J = 7.0 Hz, 8H), 3.14 (q, J = 7.0 Hz, 8H), 7.26-7.40 (m, 3H), 7.87-7.91 (m, 2H). ^{13}C NMR (C_6D_6): δ 1.57, 14.63, 14.88, 39.49, 39.84, 127.72, 128.79, 135.63, 141.59. ^{29}Si NMR (C_6D_6): δ -10.05, 14.80. MS: m/e 436 (M^+, 10), 249 ($(Et_2N)_2PhSi^+$, 73), 187 ($(Et_2N)_2MeSi^+$, 100). IR (KBr): 2975, 2940, 2860, 1375, 1202, 1175, 1022, 928. Anal. Calcd for $C_{23}H_{48}N_4Si_2$: C, 63.24, H, 11.08. Found: C, 63.14, H, 11.25.

1,1,2,2-Tetrakis(diethylamino)-1,2-dimethyldisilane (5)[12b], additional data.

^{13}C NMR (C_6D_6): δ 1.12, 15.43, 39.83. ^{29}Si NMR (C_6D_6): δ -10.87. MS: m/e 374 (M^+, 5), 187 ($(Et_2N)_2MeSi^+$, 100). IR (neat): 2960, 2925, 2850, 1370, 1200, 1175, 1020, 925.

X-ray Crystal Structure Analysis of 3

The single crystals were obtained by recrystallization from dichloromethane. Intensity data were collected on Mac Science MXC3 diffractometer using an ω-2θ scan technique, and unique reflections within $3 \leq 2\theta \leq 130°$ were collected. The structure was solved by the direct method[15] and refined anisotropically by the full-matrix least-squares method. The thermal parameter of each hydrogen atom was assumed to be isotropic and equal to that of the bonded atom. The crystal data and analytical condition, and final atomic coordinates and isotropic temperature factors are listed in Tables 3 and 4, respectively.

UV spectra of 3 in solid state

The UV spectrum was measured on a KBr pellet of **3** with no reference and the absorbance was uncorrected. The concentration of the sample was 2.7×10^{-6} mol / cm^3 and the pellet had a 0.70 mm thickness. KBr (crystal) was purchased from Shimadzu.

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Part II

(Alkoxysilyl)lithiums

Chapter 6

The Chemistry of Silylenoids: Preparation and Reactivity of (Alkoxysilyl)lithiums

Abstract: Reported herein are the first results of silylenoid chemistry, analogous to carbenoid chemistry. (*tert*-Butoxysilyl)lithium (*t*-BuO)Ph_2SiLi (**1**) prepared from (*tert*-butoxysilyl)stannane with *n*-BuLi in THF is stable at −78 °C. In the presence of 12-crown-4, **1** is stable as silyl anion even at 0 °C and reacts with electrophiles only. In contrast to this, **1** exhibits the ambiphilic reactivity and undergoes at 0 °C self-condensation smoothly to form (*t*-BuO)Ph_2Si-Ph_2SiLi or butylation in the presence of an excess amount of *n*-BuLi and TMEDA to form (*n*-Bu)Ph_2SiLi. The ambiphilic reactivities of **1** could be accounted for by contribution of two extreme structures, that is, a nucleophilic silylenoid structure and an electrophilic silylenoid structure. In the latter, the electropositive lithium atom bound to silicon ionizes and activates the silicon-oxygen bond so that the silicon becomes susceptible to the nucleophilic attack.

Introduction

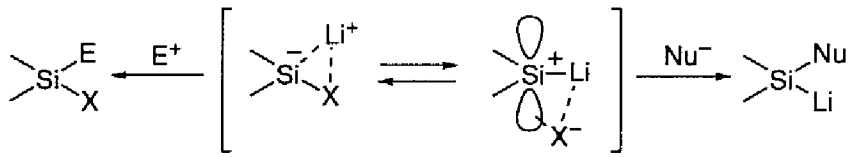
Over the past few decades a considerable number of studies have been made on *carbenoids*, [1] namely, α-heteroatom-substituted organometallics showing both nucleophilicity and electrophilicity. In contrast to this, the silicon analogues *silylenoids* [2] have been much less extensively studied so far.

Only one theoretical study has been performed on a (lithium)(fluoro)silylenoid SiH_2LiF.[3] The result suggests that the Si-F bond is weakend when lithium is attached to the silicon atom, resulting in the appearance of a positive charge on silicon. Some experimental reports have postulated silylenoids $R_2Si(X)M$ without evidence as reaction intermediates in reduction of dihalosilanes R_2SiX_2 with alkali metals M, especially in polysilane synthesis.[4] Reactivities of silylenoids, however,

have never been investigated. Study on silylenoids may thus shed a new light on the mechanism of the polysilane synthesis.

We now report the first experimental aspects of the *silylenoid* chemistry (Scheme 1) in (alkoxysilyl)lithiums.[5] The previously reported (aminosilyl)lithiums were stable functionalized silyl anions[6] and did not exhibit silylenoid character.[7] On considering the thermodynamic stability and kinetic lability of substituents, (alkoxysilyl)lithiums[8] have been expected to behave as silylenoid. Our special attention has been focused on the electrophilic nature of the (alkoxysilyl)lithiums as the most diagnostic clue to the silylenoid character, in agreement with the theoretical prediction. The results described herein may be regarded as the silicon version of the chemistry of lithium (alkoxy)carbenoids reported by Wittig in 1957.[1g]

Scheme 1



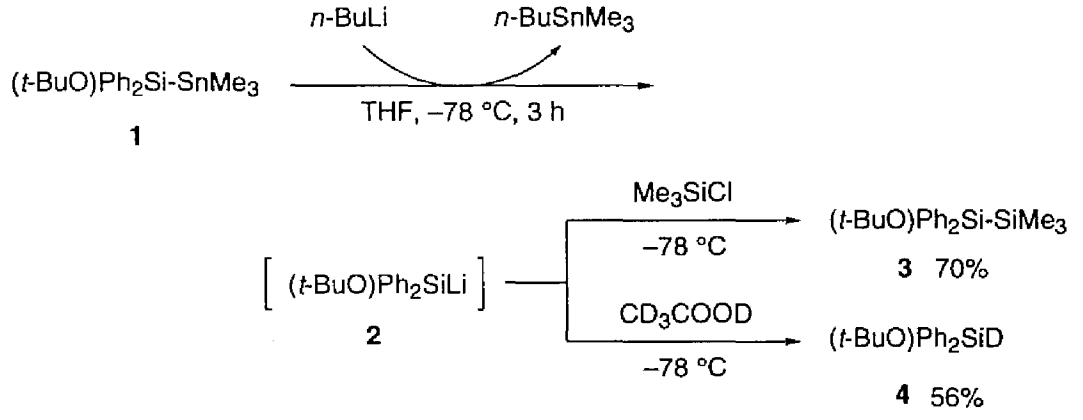
nucleophilic silylenoid — electrophilic silylenoid

Results and Discussion

A tin-lithium exchange reaction[6,9] at low temperature is of the essence for the preparation of [(*tert*-butoxy)diphenylsilyl]lithium (**2**), as shown in Scheme 2.[10] Thus, (*tert*-butoxy)silylstannane **1** was allowed to react with 2 equiv of *n*-BuLi in THF at −78 °C for 3 h to give the (*tert*-butoxysilyl)lithium **2** as a yellow solution, which was trapped with Me_3SiCl and acetic acid-d_4 to the corresponding disilane **3** in 70% yield and the deuterated silane **4** in 56% yield, respectively. The (alkoxy)silyllithium **2** was stable at −78 °C for at least 6 h, giving the trapped product **3** in 66% yield, but it underwent self-condensation almost completely at 0 °C

within 2 h (see below). This finding is a striking contrast to the high stability of the (aminosilyl)lithiums, which are stable at 0 °C for several days.[6]

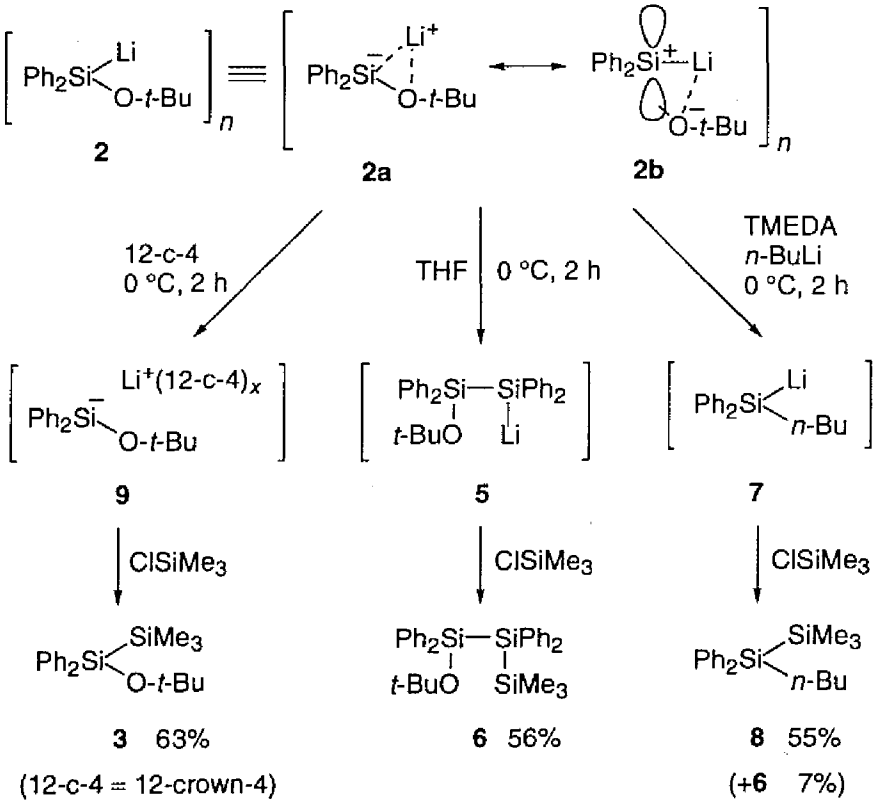
Scheme 2



The ^{29}Si NMR chemical shift of (*t*-BuO)Ph_2SiLi **2** was observed at δ 11.3 ppm at −80 °C in THF, the large downfield shift compared to the corresponding chlorosilane (*t*-BuO)Ph_2SiCl (δ −23.3 ppm) (Δδ = +34.6 ppm). This shift exhibits a remarkable contrast to the upfield shift of ordinary triorganosilyllithiums compared to chlorosilanes as examplified by $Ph_2MeSiLi$ (δ −20.5 ppm) and (δ 10.0 ppm) (Δδ = −30.5 ppm).[12] It is noteworthy that the large downfield shift is reminiscent of the well-known ^{13}C NMR behavior of carbenoids.[1d,e,h]

The ambiphilic reactivities of **2** have been disclosed by analysis of the decomposition products, as summarized in Scheme 3. At 0 °C, **2** underwent bimolecular self-condensation smoothly, via nucleophilic substitution of the *tert*-butoxy group by another molecule of silyllithium, to give [2-(*tert*-butoxy)disilanyl]lithium **5**, which afforded (*tert*-butoxy)trisilane **6** in 56% yield by trapping with Me_3SiCl: Note that one molecule of **2** behaves as a nucleophile and the other as an electrophile. Generation of **5** was confirmed by the ^{29}Si NMR spectrum at 0 °C showing two signals at δ −43.7 ppm for the lithium-bearing silicon and −2.3 ppm.[12]

Scheme 3



Nucleophilic butylation of **2** with external *n*-BuLi (5 equiv to **1**) in the presence of TMEDA (7 equiv to **1**) occurred concomitantly to afford butyldiphenylsilyllithium **7**. Upon trapping with Me_3SiCl, **7** gave the corresponding disilane **8**, in addition to the self-condensation product **6**.[13] The ratio **8/6** was 89/11 (62% total yield).[14] It has been confirmed that in the presence of TMEDA but in the absence of *n*-BuLi, **2** undergoes the self-condensation mainly at 0 °C for 2 h to form **6** in 51% yield, together with a small amount of **3** (7%), indicative of the preservation of the ambiphilic character of **2**.

The ambiphilic reactivity of **2** disappears completely by addition of a crown ether which is expected to make a "solvent-separated ion pair" **9**[1f] (Scheme 3). Thus, in the presence of 2 equiv of 12-crown-4,[15] the (alkoxy)silyl anion **9** was

stable even at 0 °C for 2 h, giving the trapped product **3** in 63% yield, and underwent neither self-condensation nor butylation at all.[16]

The ambiphilic reactivities of **2** could be accounted for by contribution of two extreme electronic structures, that is, a nucleophilic silylenoid structure **2a** and an electrophilic silylenoid structure **2b**,[3] as shown in Scheme 3, by analogy with the carbenoid chemistry.[1] In the latter **2b**, the electropositive lithium atom bound to silicon ionizes and activates the silicon-oxygen bond,[17] so that the silicon becomes more susceptible to the nucleophilic attack than that in the ordinary neutral alkoxysilanes. The ^{29}Si NMR chemical shift for **2** in the lower field supports the contribution of the electrophilic structure.

Some control experiments offered supporting evidence for the activation of the silicon-oxygen bond in **2**. A counter model (*t*-BuO)Ph_2SiMe, containing the neutral methyl group instead of the cationic lithium atom,[18] was hardly butylated with *n*-BuLi (5 equiv) to form (*n*-Bu)Ph_2SiMe in only 4% yield at 0 °C for 10 min in THF in the presence of TMEDA (5 equiv). Under the same conditions, **2** was butylated to give **8** in 24% yield, together with 9% of **6**. Furthermore, (*t*-BuO)Ph_2SiMe hardly reacted with **2** (1 equiv) or $PhMe_2$SiLi (10 equiv) at 0 °C for 2 h to give essentially no silylated product (*t*-BuO)$Ph_2SiSiMe_2Ph$ or $PhMe_2SiSiMePh_2$, under which conditions **2** itself underwent the self-condensation completely. The *t*-BuO–Si bond in **2** is thus much more reactive than that in the model compound towards the nucleophiles.

No *free* silylene[2] appears to be generated under the present conditions. In the presence of various trapping agents such as diethylmethylsilane, diphenylacetylene, and 2,3-dimethylbutadiene, no silylene-trapped products were obtained.[8,19]

Two further points deserve comment. First, the ambiphilicity of silylenoid allows the successive introduction of a nucleophile and of an electrophile to a silylene moiety.[20] The important point to be noted is that a nucleophile is introduced first with ease because of the high electrophilicity of silylenoid, which makes a sharp contrast to the conventional transformations involving simple silyl anions where only an electrophile is introduced. This new reaction pattern may thus suggest potential synthetic utility of silylenoids.

Second, the reactivity of silylenoid may offer a new clue to the elucidation of the mechanism of silicon chain elongation reactions in polysilane synthesis via reductive coupling of dihalosilanes (R_2SiX_2) with alkali metal (M).[4,21] The present results thus strongly suggest a possibility for the direct conversion of the initially formed silylenoid species $R_2Si(X)(M)$ into a β-halodisilanyl-metal species $(X)R_2SiSiR_2(M)$ via self-condensation: The process has never been proposed for the mechanism of polysilane synthesis.[4,21,22]

Experimental Section

General Remarks. ^1H (200 MHz), ^{13}C (50.29 MHz) NMR spectra were recorded on a Varian VXR-200 spectrometer. ^1H and ^{13}C chemical shifts are referenced to internal benzene-d_6 (^1H δ 7.200 ppm and ^{13}C δ 128.00 ppm). ^{29}Si (53.67 MHz) NMR spectra were recorded on a JEOL EX-270 spectrometer. The ^{29}Si NMR spectra were observed in an unlocked mode at −80 °C for **2** and at 0 °C for **5** after the spectrometer was zeroed by using a Me_4Si/THF−THF-d_8 sample at −80 °C and at 0 °C, respectively. Although the spectrometer was unlocked during the acquisition, the field was stable and no significant field shift was observed by reconfirmation of the chemical shift of Me_4Si/THF−THF-d_8 after the acquisition. The anions were prepared previously in THF as described in the experimental procedure and the resulting solution was transferred to an NMR sample tube via a Teflon tube under an argon atmosphere. Mass spectra were measured at 70 eV on a JEOL JMS-DX300 mass spectrometer equipped with a JMA-3500 data processing system. Melting points were measured with a Yanaco-MP-S3 apparatus and were uncorrected. The elemental analyses were performed at the Microanalysis Division of Institute for Chemical Research, Kyoto University: Analytical samples were purified by preparative GLC, preparative HPLC, or recrystallization. GLC analysis was performed on a Shimadzu GC-4B gas chromatographed, equipped with a 3-m or 1-m column packed with 30% Silicone DC550 on celite 545. Column chromatography was performed by using Kieselgel 60 (70−230 mesh) (Merck).

Thin layer chromatography (TLC) was performed on plates of silica gel 60F-254 (Merck).

Trimethylchlorostannane was prepared by disproportionation between tetramethylstannane and dimethyldichlorostannane:[23] the last was kindly donated from the Nitto Kasei Co. THF was distilled under nitrogen from sodium/benzophenone. Triethylamine and *tert*-butyl alcohol were distilled from calcium hydride. Tetramethylethylenediamine (TMEDA) was distilled from *n*-butyllithium. 12-crown-4 was purchased from Aldrich and dried over Molecular Sieves 3A before use. Lithium granular was purchased from Chemetall Gesellshaft. *n*-Butyllithium in hexane was purchased from Wako Pure Chemical Industries. All reactions were carried out under an argon atmosphere.

(*tert*-Butoxy)diphenylchlorosilane. To a mixture of diphenyldichlorosilane (41.0 mL, 200 mmol) and triethylamine (42.0 mL, 300 mmol) in THF (150 mL) was added a solution of *tert*-butyl alcohol (28.0 mL, 300 mmol) in THF (15 mL) over 30 min at 0 °C. Then the mixture was refluxed for 55 h. The solution was diluted with hexane and the precipitated salts were filtered off. The filtrate was concentrated and the residue was distilled through a short path column (138–151 °C/2.0 mmHg) to give the title compound (44.3 g, 76% yield) as colorless oil. ^{1}H NMR (C_6D_6): δ 1.31 (s, 9H), 7.16–7.20 (m, 6H), 7.83–7.88 (m, 4H). ^{13}C NMR (C_6D_6): δ 31.69, 76.39, 128.20, 130.79, 134.72, 135.26. MS: *m/e* 292 (M^++2, 4), 290 (M^+, 11), 277 (M^++2–Me, 30), 275 (M^+–Me, 79), 363 (M^++2–*t*-BuO, 35), 217 (M^+–*t*-BuO, 100), 197 (9), 181 (16), 157 (37). Anal. Calcd for $C_{15}H_{19}OSiCl$: C, 66.07; H, 6.58. Found: C, 65.92; H, 6.76.

[(*tert*-Butoxy)diphenylsilyl]trimethylstannane (1). (1) Trimethylstannyllithium was prepared by the literature method[24] from trimethylstannyl chloride (15.09 g, 75.7 mmol) with lithium granular (3.33 g, 480 mmol) in THF (85 mL). The resulting solution was used in the next step without titration after removal of the unreacted lithium. (2) To a solution of (*tert*-butoxy)diphenylchlorosilane (19.88 g, 68.3 mmol) in THF (30 mL) was added the

THF solution of trimethylstannyllithium over 50 min at 0 °C and the mixture was stirred at 0 °C for 45 min and at room temperature for 14 h. The reaction mixture was evaporated , diluted with hexane, and filtered. The filtrate was concentrated and the residue was distilled through a short path column (153-160 °C/2.0 mmHg) to give **1** (22.71 g, 79%) as colorless oil. ^{1}H NMR (C_6D_6): δ 0.34 (s, 9H), 1.29 (s, 9H), 7.20-7.25 (m, 6H), 7.74-7.79 (m, 4H). ^{13}C NMR (C_6D_6): δ -10.06, 32.09, 73.68, 128.29, 129.76, 134.68, 139.80. MS: *m/e* 420 (M^+, 1), 416 (M^+-Me, 4), 363 (M^+-*t*-Bu, 1), 255 ((*t*-BuO)Ph_2Si^+, 14), 199 (100). mp 52.0-53.5 °C. Anal. Calcd for $C_{19}H_{28}OSiSn$: C, 54.44; H, 6.73. Found: C, 54.33; H, 6.83.

[(*tert*-Butoxy)diphenylsilyl]lithium (2). To a solution of **1** (312 mg, 0.744 mmol) in THF (3.0 mL) was added dropwise over 1 min a hexane solution of *n*-BuLi (1.64 M, 0.91 mL, 1.5 mmol) at -78 °C and the solution was stirred for 3 h to give a yellow solution of **2**.

1-*tert*-Butoxy-1,1-diphenyl-2,2,2-trimethyldisilane (3). To a THF solution of **2**, prepared from **1** (0.744 mmol) and *n*-BuLi (1.5 mmol) in THF (3.0 mL), was added trimethylchlorosilane (0.21 mL, 1.6 mmol) at -78 °C. After stirring for 30 min, the solution was warmed to the ambient temperature. The solution was analyzed directly by GLC and the yield of **3** was estimated (70%) by using docosane as internal standard. The pure sample of **3** was obtained as colorless oil by preparative GLC. ^{1}H NMR (C_6D_6): δ 0.28 (s, 9H), 1.26 (s, 9H), 7.24-7.28 (m, 6H), 7.76-7.81 (m, 4H). ^{13}C NMR (C_6D_6): δ -1.22, 32.30, 73.34, 128.09, 129.51, 135.31, 139.20. MS: *m/e* 328 (M^+, 1), 313 (M^+-Me, 1), 255 (M^+-$SiMe_3$, 7), 199 (100). Anal. Calcd for $C_{19}H_{28}Si_2$: C, 69.45; H, 8.59. Found: C, 69.55; H, 8.59.

(*tert*-Butoxy)diphenyldeuteriosilane (4). To a solution of **2**, prepared from **1** (0.537 mmol) and *n*-BuLi (1.1 mmol) in THF (2.0 mL), was added acetic acid-d_4 (0.12 mL, 1.4 mmol). After stirring at -78 °C for 20 min, a 10% aq. solution of NH_4Cl (3.0 mL) was added. The solution was warmed to the ambient

temperature. The reaction mixture was extracted with Et_2O (10 mL x 3). The combined organic layer was washed with a 10% aq. solution of $NaHCO_3$ (10 mL) and water (10 mL), and dried over Na_2SO_4. The solution was concentrated in vacuo to yield crude **4**. The yield of **4** was estimated by GLC analysis (56%): Eicosane was used as internal standard. The pure sample of **4** was obtained as colorless oil by preparative GLC. ^1H NMR (C_6D_6): δ 1.29 (s, 9H), 7.20–7.24 (m, 6H), 7.73–7.78 (m, 4H). ^{13}C NMR (C_6D_6): δ 31.56, 73.57, 128.19, 130.17, 134.89, 136.49. MS: *m/e* 257 (M^+, 48), 255 (M^+–D, 4), 242 (M^+–Me, 76), 199 (69), 184 (M^+–*t*-BuO, 100), 178 (M^+–PhD, 77), 124 (34), 123 (46), 122 (46).

(*tert*-Butoxy)diphenylsilane. ^1H NMR (C_6D_6): δ 1.30 (s, 9H), 5.85 (s, 1H), 7.20–7.25 (m, 6H), 7.74–7.79 (m, 4H). ^{13}C NMR (C_6D_6): δ 31.56, 73.60, 128.20, 130.17, 134.90, 136.53. MS: *m/e* 256 (M^+, 11), 255 (M^+–H, 2), 241 (M^+–Me, 54), 199 (M^+–*t*-Bu, 65), 183 (M^+–*t*-BuO, 99), 178 (100), 123 (77). Anal. Calcd for $C_{16}H_{20}OSi$: C, 74.95; H, 7.86. Found: C, 74.76; H, 7.72.

1-*tert*-Butoxy-1,1,2,2-tetraphenyl-3,3,3-trimethyltrisilane (6). A solution of **2**, prepared from **1** (0.800 mmol) with *n*-BuLi (1.6 mmol) in THF (2.0 mL), was allowed to warm to 0 °C and stirred for 2 h, followed by addition of trimethylchlorosilane (0.22 mL, 1.8 mmol). The solution was stirred at 0 °C for 1 h and then warmed to room temperature. A 5% aq. solution of NH_4Cl (5 mL) was poured into the mixture. The mixture was extracted with Et_2O (10 mL x 3). The combined organic layer was washed with water (10 mL) and brine (10 mL), and dried over $MgSO_4$. The solution was concentrated to yield crude **6**. The yield of **6** was estimated by means of ^1H NMR analysis (56%): Mesitylene was used as internal standard. The pure sample of **6** was obtained as colorless oil by silica gel column chromatography (hexane/CH_2Cl_2 = 10/1, R_f = 0.46). ^1H NMR (C_6D_6): δ 0.24 (s, 9H), 1.28 (s, 9H), 7.14–7.20 (m, 12H), 7.76–7.83 (m, 8H). ^{13}C NMR (C_6D_6): δ –0.51, 32.24, 75.39, 128.00, 128.12, 128.77, 129.78, 135.90, 136.97 , 138.54 MS: *m/e* 510 (M^+, 1), 453 (M^+–*t*-Bu, 37), 437 (M^+–$SiMe_3$, 1), 255

(8), 240 (9), 199 (100). Anal. Calcd for $C_{31}H_{38}Si_3$: C, 72.88; H, 7.50. Found: C, 72.63; H, 7.48.

Reaction of 2 with *n*-BuLi. To a solution of **2**, prepared from **1** (0.650 mmol) with *n*-BuLi (1.3 mmol) in THF (2.0 mL), was added TMEDA (0.69 mL, 4.6 mmol) at −78 °C and the mixture was stirred for 15 min. Then *n*-BuLi in hexane solution (1.70 M, 1.91 mL, 3.25 mmol) was added over 1 min. After 5 min the solution was allowed to warm to 0 °C and stirred for 2 h, followed by addition of trimethylchlorosilane (0.63 mL, 5.0 mmol). After warming to room temperature, a 5% aq. solution of NH_4Cl (5 mL) was poured into the mixture, which was extracted with Et_2O (10 mL x 3). The combined organic layer was washed with water (10 mL) and brine (10mL), and dried over $MgSO_4$. The solution was concentrated in vacuo. Purification by silica gel column chromatography (hexane/AcOEt = 100/1) gave pure **8** (111 mg, 55%, R_f = 0.55) and crude **6** (R_f = 0.19). The yield of **6** was estimated by means of ^1H NMR analysis (7%): Mesitylene was used as internal standard.

1-*n*-Butyl-1,1-diphenyl-2,2,2-trimethyldisilane (8). ^1H NMR (C_6D_6): δ 0.24 (s, 9H), 0.88 (t, J = 7.0 Hz, 9H), 1.21-1.60 (m, 6H), 7.23-7.28 (m, 6H), 7.60-7.64 (m, 4H). ^{13}C NMR (C_6D_6): δ 1.03, 12.97, 13.85, 27.11, 27.34, 128.26, 129.08, 135.64, 136.87. MS: *m/e* 312 (M^+, 24), 297 (M^+-Me, 1), 255 (M^+-*n*-Bu, 10), 239 (M^+-$SiMe_3$, 24), 183 (100). Anal. Calcd for $C_{19}H_{28}Si_2$: C, 73.00; H, 9.03. Found: C, 72.77; H, 8.84.

Preparation of 9, followed by trapping with Me_3SiCl. To a solution of **2**, prepared from **1** (0.606 mmol) with *n*-BuLi (1.21 mmol) in THF (2.0 mL), was added 12-crown-4 (0.20 mL, 1.21 mmol) at −78 °C and the solution was stirred vigorously for 25 min to yield an orange solution of **9**. The solution was allowed to warm to 0 °C and stirred for 2 h, followed by addition of trimethylchlorosilane (0.53 mL, 4.2 mmol). After stirring for 30 min, the solution was warmed to room temperature. Then a 5% aq. solution of NH_4Cl (10 mL) was

poured into the mixture. The mixture was extracted with Et_2O (10 mL x 3). The combined organic layer was washed with water (10 mL) and brine (10 mL), and dried over $MgSO_4$, and concentrated in vacuo to yield crude **3**. The yield of **3** was estimated by GLC analysis (63%).

(*tert*-Butoxy)(diphenyl)methylsilane. To a solution of diphenyl(methyl)chlorosilane (5.16 mL, 25.0 mmol), triethylamine (4.53 mL, 32.5 mmol), and 4-(dimethylamino)pyridine (306 mg, 2.50 mmol) in THF (50 mL) was added a solution of *tert*-butyl alcohol (2.83 mL, 30.0 mmol) in THF (3 mL) over 8 min at room temperature and the mixture was stirred overnight. The mixture was diluted with *n*-hexane (50 mL) and the precipitated salts were filtered off. The filtrate was concentrated and the residue was diluted with Et_2O (30 mL), washed with 0.5 M HCl (20 mL x 2), water (20 mL), and brine (20 mL), and dried over $MgSO_4$. Bulb-to-bulb distillation (110–130 °C/0.45 mmHg) gave the titled compound (5.67 g, 84%) as colorless oil. ^1H NMR (C_6D_6): δ 0.69 (s, 3H), 1.24 (s, 9H), 7.23–7.27 (m, 6H), 7.71–7.76 (m, 4H). ^{13}C NMR (C_6D_6): δ 0.32, 32.18, 73.36, 128.00, 129.63, 134.69, 139.03. MS: *m/e* 270 (M^+, 25), 255 (M^+–Me, 100), 199 (103), 197 (M^+–*t*-BuO, 80), 181 (11), 137 (39). Anal. Calcd for $C_{15}H_{19}OSiCl$: C, 75.50; H, 8.34. Found: C, 75.21; H, 8.34.

Reaction of (*tert*-Butoxy)(diphenyl)methylsilane with *n*-BuLi. To a solution of (*tert*-butoxy)(diphenyl)methylsilane (139 mg, 0.514 mmol) and TMEDA (0.39 mL, 2.6 mmol) in THF (2.0 mL) was added *n*-BuLi in hexane solution (1.64 M, 1.57 mL, 2.57 mmol) at −78 °C and the mixture was stirred for 5 min. The reaction mixture was allowed to warm to 0 °C. After 10 min the reaction was quenched at 0 °C with Me_3SiCl (0.36 mL, 2.8 mmol). After evaporation of the volatile materials, the residue was diluted with hexane (10 mL), filtered, and evaporated. Bulb-to-bulb distillation (130–140 °C/0.51 mmHg) gave a mixture of recoverd (*tert*-butoxy)(diphenyl)methylsilane (96% yield) and (*n*-butyl)(diphenyl)methylsilane (4% yield) (total 140 mg). The yields of the products were estimated by ^1H NMR analysis. The ^1H chemical shifts of (*n*-

butyl)(diphenyl)methylsilane were coincident with those of the authentic sample, which was prepared by the reaction of $Ph_2MeSiCl$ with *n*-BuLi in THF.

Reaction of (*tert*-Butoxy)(diphenyl)methylsilane with $PhMe_2SiLi$. To a solution of (*tert*-butoxy)(diphenyl)methylsilane (112 mg, 0.414 mmol) in THF (2.0 mL) was added a solution of dimethylphenylsilyllithium in THF (0.54 M, 7.6 mL, 4.1 mmol) at −78 °C. After stirring at −78 °C for 5 min, the reaction solution was allowed to warm to 0 °C. After 2 h the reaction was quenched at 0 °C by addition of a 10% aq. solution of NH_4Cl (5 mL) and worked up in the usual way. Purification by silica gel column chromatography (hexane, $R_f = 0.20$) and ^1H NMR analysis showed the formation of 1% yield of 1,1,2-trimethyl-1,2,2-triphenyldisilane. The ^1H NMR chemical shifts were coincident with those of the authentic sample, which was prepared by the reaction of $PhMe_2SiLi$ with $Ph_2MeSiCl$ in THF. ^1H NMR (C_6D_6): δ 0.43 (s, 6H), 0.62 (s, 3H), 7.16–7.21 (m, 9H), 7.41–7.46 (m, 2H), 7.52–7.57 (m, 4H).

Reaction of (*tert*-Butoxy)(diphenyl)methylsilane with 2. To a THF solution of **2**, prepared from **1** (0.515 mmol) and *n*-BuLi (1.03 mmol) in THF (2.0 mL), was added a solution of (*tert*-butoxy)(diphenyl)methylsilane (139 mg, 0.515 mmol) in THF (2.0 mL) at −78 °C. After stirring for 5 min, the solution was warmed to 0 °C. After 2 h the reaction was quenched at 0 °C by addition of trimethylchlorosilane (0.14 mL, 1.1 mmol) and worked up in the usual way. ^1H NMR analysis showed the formation of no 1-*tert*-butoxy-2-methyl-1,1,2,2-tetraphenyldisilane.

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Chapter 7

Reduction of Phenylchlorosilanes with Lithium 1-(Dimethylamino)naphthalenide: A New Access to Functionalized Silyllithiums

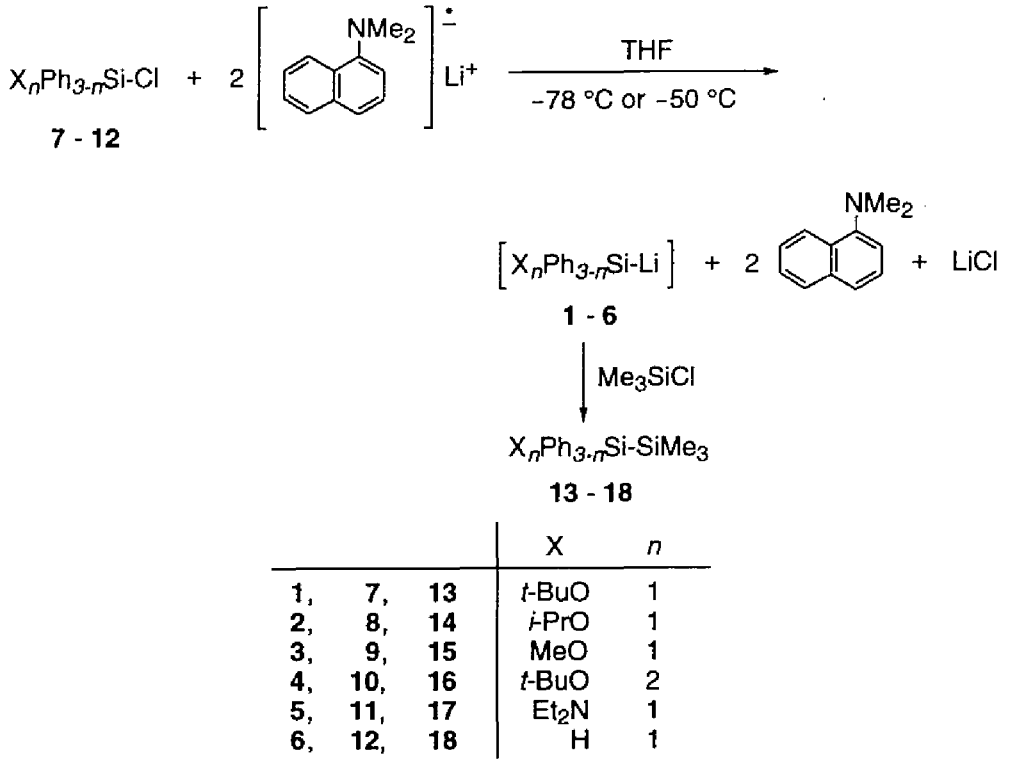
Abstract: Reduction of alkoxy-, amino-, and hydrochlorosilanes with lithium 1-(dimethylamino)naphthalenide at low temperatures gives the corresponding alkoxy-, amino-, and hydrosilyllithiums, respectively. Electrophilicity of (dialkoxysilyl)lithium extremely decreases in contrast to that of (monoalkoxysilyl)lithiums.

Intoduction

In the course of the systematic studies on functionalized silyllithiums,[1,2] the author has prepared an (alkoxysilyl)lithium (*t*-BuO)Ph_2SiLi (**1**) by tin-lithium exchange reaction of a silylstannane (*t*-BuO)Ph_2Si-$SnMe_3$ and found that **1** exhibits both nucleophilicity and electrophilicity, that is, silylenoid character (Chapter 6):[1] The silyllithium **1** undergoes self-condensation or butylation by external nucleophile *n*-BuLi. This finding prompted the author to investigate the reactivity of various (alkoxysilyl)lithiums.[3] The tin-lithium exchange reaction of silylstannanes, however, could not be applicable to preparation of silyllithiums with small functional groups because the reaction depends on steric bulkiness around the central silicon atom.[4] Although reduction of chlorosilane with lithium metal,[5] more conventional method, is independent of the steric bulkiness, the reaction usually proceeds above 0 °C, at temperatures at which (alkoxysilyl)lithiums might be not stable.[1] Thus, the author had to develop a more widely applicable mild method for preparation of various (alkoxysilyl)lithiums.

Reported herein is a new access to functionalized silyllithiums. Lithium 1-(dimethylamino)naphthalenide (LDMAN) is an efficient reductant of chlorosilanes to afford various alkoxy- and other functionalized silyllithiums (Scheme 1).

Scheme 1



	X	*n*
1, 7, 13	*t*-BuO	1
2, 8, 14	*i*-PrO	1
3, 9, 15	MeO	1
4, 10, 16	*t*-BuO	2
5, 11, 17	Et_2N	1
6, 12, 18	H	1

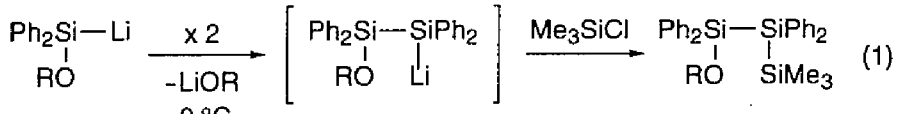
Results and Discussion

Three reductants, lithium naphthalenide (LiNp), lithium 4,4'-di-*tert*-butylbiphenylide (LDBB), and LDMAN have been examined first:[6,7] Reduction of a chlorosilane (*t*-BuO)Ph_2SiCl (**7**) with LiNp gave silyllithium (*t*-BuO)Ph_2SiLi (**1**) and homocoupling disilane [(*t*-BuO)Ph_2Si-]$_2$ in the ratio of 80:20.[8] The homocoupling could not be avoided even by slow addition of **7** to an excess amount of LiNp solution at -78 °C. Stronger reductants LDBB and LDMAN, however, suppressed the homocoupling reaction almost completely (>98:<2). LDMAN is reagent of choice since the resulting basic 1-(dimethylamino)naphthalene can be readily separated from the final products by extraction or column chromatography. The generation of **1** was confirmed by ^{29}Si NMR analysis. A signal was observed at 10.0 ppm, which is consistent with the value described in Chapter 6.[1]

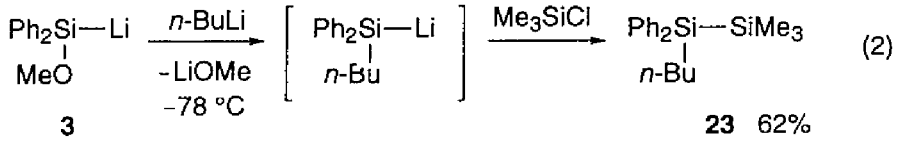
Table 1 summarizes representative results. In general procedures, a chlorosilane (**7** - **12**) was added to a solution of excess amount of LDMAN (4.5 equiv) in THF at -78 °C to -50 °C. The resulting silyllithium (**1** - **6**) was trapped with Me_3SiCl to form the corresponding disilane (**13** - **18**). In addition to the tertiary (alkoxysilyl)lithium **1** (entries 1 and 2), secondary and primary alkoxy analogs, (*i*-PrO)Ph_2SiLi (**2**) and (MeO)Ph_2SiLi (**3**), were obtained at -78 °C within 15 min in good yields (entries 3 and 4). They must be prepared at low temperature to suppress the self-condensation and/or decomposition. The order of the yields did not reflect directly the bulkiness of the alkoxy groups. Preparation of (dialkoxysilyl)lithium (*t*-BuO)$_2$PhSiLi (**4**) required the higher temperature (-50 °C) (entry 5). No reduction occurred at -78 °C and the starting chlorosilane **10** was recovered. The (aminosilyl)lithium (Et_2N)Ph_2SiLi (**5**) was also prepared in good but somewhat lower yield (82%) at -50 °C (entry 7) than that obtained by reduction of the chlorosilane **11** with lithium metal (98%).[2] A (hydrosilyl)lithium HPh_2SiLi (**6**) was obtained in moderate yield (40%) (entry 8); the yield is however higher than that by the Gilman's procedure (11%).[9]

Reduction of a disilanyl chloride (Me_3Si)Ph_2SiCl (**19**) gave the homocoupling tetrasilane [(Me_3Si)Ph_2Si-]$_2$ (**20**) in 52% yield without detection of trapping product of the corresponding (disilanyl)lithium (entry 9).[10] Attempted reduction of methylchlorosilane analogs XMe_2SiCl (X = Me, *t*-BuO, and Et_2N) afforded neither silyllithiums nor homocoupling disilanes.[11]

As reported previously,[1] (*t*-BuO)Ph_2SiLi (**1**) underwent self-condensation at 0 °C for 2 h to give, after trapping with Me_3SiCl, a trisilane **21** (48% yield) via a [2-(alkoxy)disilanyl]lithium, in addition to the disilane **13** (25% yield) (eq. 1). The methoxy analog (MeO)Ph_2SiLi (**3**) also underwent self-condensation similarly but more rapidly at 0 °C within 10 min to give a trisilane (MeO)Ph_2Si-Ph_2Si-$SiMe_3$ (**22**) in 29% yield, together with the disilane **15** in 9% yield (eq. 1). The methoxy derivative **3** also underwent butylation with *n*-BuLi even at -78 °C within 30 min to afford (*n*-Bu)Ph_2Si-$SiMe_3$ (**23**) in 62% yield after trapping with Me_3SiCl (eq. 2). Thus, **3** exhibits both nucleophilicity and electrophilicity even at -78 °C.



(1)



(2)

The (dialkoxysilyl)lithium (t-BuO)$_2$PhSiLi (**4**) is more stable than the (monoalkoxysilyl)lithiums **1**-**3**. When the solution of **4**, prepared at -50 °C, was allowed to warm to 0 °C followed by trapping with Me_3SiCl after 2 h, the author obtained the simply trapped disilane **16** in 76% yield. The expected self-condensation product (t-BuO)$_2$PhSi-(t-BuO)PhSi-$SiMe_3$ was not detected even after longer reaction time was employed. In addition, **4** did not undergo butylation with n-BuLi at 0 °C for 2 h to give here again **16** only in 73% yield after trapping with Me_3SiCl.

Thus the author developed the new method for preparation of alkoxy-, amino-, and [hydro(phenyl)silyl]lithiums by reduction of the corresponding chlorosilanes with LDMAN at low temperatures. The successful preparation of primary and secondary (alkoxy)silyllithiums and (dialkoxysilyl)lithium may shed a new light on the silylenoid chemistry.

Table 1. Reduction of Functionalized Chlorosilanes wih LDMAN, followed by Trapping with Me_3SiCl[a]

entry	chlorosilane	conditions	silyllithiums	trapping product, yield (%)[b,c]
1	(*t*-BuO)Ph_2SiCl (**7**)	−78 °C, 15 min	(*t*-BuO)Ph_2SiLi (**1**)	(*t*-BuO)$Ph_2SiSiMe_3$ (**13**) 81[d]
2	(*t*-BuO)Ph_2SiCl (**7**)	−78 °C, 15 min[e]	(*t*-BuO)Ph_2SiLi (**1**)	(*t*-BuO)$Ph_2SiSiMe_3$ (**13**) 67[d]
3	(*i*-PrO)Ph_2SiCl (**8**)	−78 °C, 15 min	(*i*-PrO)Ph_2SiLi (**2**)	(*i*-PrO)$Ph_2SiSiMe_3$ (**14**) 46
4	(MeO)Ph_2SiCl (**9**)	−78 °C, 15 min	(MeO)Ph_2SiLi (**3**)	(MeO)$Ph_2SiSiMe_3$ (**15**) 77
5	(*t*-BuO)$_2$PhSiCl (**10**)	−50 °C, 1 h	(*t*-BuO)$_2$PhSiLi (**4**)	(*t*-BuO)$_2$PhSiSiMe$_3$ (**16**) 93
6	(Et_2N)Ph_2SiCl (**11**)	−78 °C, 15 min	(Et_2N)Ph_2SiLi (**5**)	(Et_2N)$Ph_2SiSiMe_3$ (**17**) 58
7	(Et_2N)Ph_2SiCl (**11**)	−50 °C, 1 h	(Et_2N)Ph_2SiLi (**5**)	(Et_2N)$Ph_2SiSiMe_3$ (**17**) 82
8	HPh_2SiCl (**12**)	−50 °C, 1 h	HPh_2SiLi (**6**)	$HPh_2SiSiMe_3$ (**18**) 40[d,f]
9	(Me_3Si)Ph_2SiCl (**19**)	−78 °C, 15 min[g]		[(Me_3Si)Ph_2Si]$_2$ (**20**) 52[d,h]

[a] Unless otherwise stated, an excess amount of LDMAN (4.5 equiv) was used.

[b] The reaction mixture was subjected to the reversed phase column chromathography to remove the resulting 1-(dimethylamino)naphthalene.

[c] The yields were estimated by GLC analysis, unless otherwise stated.

[d] The reaction mixture was washed with 1 M hydrochloric acid followed by extraction with Et_2O to remove 1-(dimethylamino)naphthalene.

[e] LDMAN (2.2 equiv).

[f] The yield was estimated by ^1H NMR analysis.

[g] No silyllithium was formed.

[h] Isolated yield.

Experimental Section

General Remarks. ^{1}H (270 MHz), ^{13}C (67.94 MHz), and ^{29}Si (53.67 MHz) NMR spectra were recorded on a JEOL EX-270 spectrometer. ^{1}H and ^{13}C chemical shifts are referenced to internal benzene-d_6 (^{1}H δ 7.200 ppm and ^{13}C δ 128.00 ppm). ^{29}Si chemical shifts are referenced to internal tetramethylsilane (0 ppm). The ^{29}Si NMR spectra were observed in an unlocked mode at −100 °C for **1**. Although the spectrometer was unlocked during the acquisition, the field was stable and no significant field shift was observed. For NMR measurements, the silyllithium **1** was prepared in THF as described in the experimental procedure and the resulting solution was transfered to an NMR sample tube via a Teflon tube under an argon atmosphere. Mass spectra were measured at 70 eV on a JEOL JMS-DX300 mass spectrometer equipped with a JMA-3500 data processing system. Melting points were measured with a Yanaco-MP-S3 apparatus and were uncorrected. The elemental analyses were performed at the Microanalysis Division of Institute for Chemical Research, Kyoto University: Analytical samples were purified by preparative GLC, preparative HPLC, or recrystallization. Analytical and preparative GLC were performed on a Shimadzu GC-4B gas chromatography, equipped with a 3-m or 1-m column packed with 30 % Silicone DC550 on Celite 545. Column chromatography was performed by using Kieselgel 60 (70-230 mesh) (Merck). Thin layer chromatography (TLC) was performed on plates of silica gel 60F-254 (Merck). Revesed-phase column chromatography was performed by using Wakogel LP-40C18 (20-40 μm) (Wako Pure Chemical Industries). Reversed-phase thin layer chromatography was performed on plates of RP-18 $F_{254}s$ (Merck).

(Diethylamino)diphenylchlorosilane was prepared by the same method as described in the literature.[12] Diphenylchlorosilane was distilled under reduced pressure before use. 1-(Dimethylamino)naphthalene was purchased from Wako Pure Chemical Industries and distilled under reduced pressure. Trimethylchlorosilane was treated with sodium cut under nitrogen to remove the dissolving HCl and the supernatant was used. *n*-Butyllithium in hexane and lithium

granular were purchased from Wako Pure Chemical Industries and Chemetall Gesellshaft, respectively. THF was distilled under nitrogen from sodium benzophenone ketyl. *tert*-Butyl alcohol, isopropyl alcohol, triethylamine, and carbon tetrachloride were distilled from calcium hydride. Methanol was distilled from magnesium methoxide. 4-(Dimethylamino)pyridine and palladium chloride were commercially available and used without further purification. All reactions were carried out under an argon atmosphere.

Preparation of starting materials (Functionalized Chlorosilanes). Bis(*tert*-butoxy)phenylchlorosilane (10). To a mixture of phenyltrichlorosilane (8.00 mL, 50.0 mmol), triethylamine (15.3 mL, 110 mmol), and 4-(dimethylamino)pyridine (305 mg, 2.5 mmol) in THF (100 mL) was added a solution of *tert*-butyl alcohol (10.4 mL, 110 mmol) in THF (10 mL) over 15 min at 0 °C. The mixture was stirred at room temperature for 6 h. The mixture was diluted with hexane (ca. 100 mL) and the salts were filtered with suction. The filtrate was concentrated and the residue was distilled through a short path column (85–91 °C/0.60 mmHg) to give **10** (9.50 g, 66% yield) as colorless oil. ^{1}H NMR (C_6D_6): δ 1.37 (s, 18H), 7.20–7.23 (m, 3H), 7.94–7.97 (m, 2H). ^{13}C NMR (C_6D_6): δ 31.56, 75.76, 128.05, 130.62, 134.38, 135.57. MS: *m/e* 288 (M^++2, 2), 286 (M^+, 2), 273 (M^++2–Me, 26), 271 (M^+–Me, 63), 217 (27), 215 (76), 159 (28), 157 (81), 57 (*t*-Bu^+, 100). Anal. Calcd for $C_{14}H_{23}O_2SiCl$: C, 58.62; H, 8.08. Found: C, 58.61; H, 8.32.

(*tert*-Butoxy)diphenylchorosilane (7). This compound[1] was prepared from diphenyldichlorosilane and *tert*-butyl alcohol in 76% yield by essentially the same method as described above.

(Isopropoxy)diphenylchlorosilane (8). Isopropyl alcohol (3.83 mL, 50.0 mmol) was added to diphenyldichlorosilane (10.4 mL, 50.0 mmol) at 0 °C. Dry nitrogen gas was bubbled through the mixture at 0 °C for 3 h and then at room temperature for 4 h. The mixture was distilled through a short path column (121–

129 °C/0.7 mmHg) to give **8** (11.9 g, <86% yield) as colorless oil with small amounts of impurities. ^{1}H NMR (C_6D_6): δ 1.17 (d, J = 6.2 Hz, 6H), 4.30 (septet, J = 6.2 Hz, 1H), 7.15-7.20 (m, 6H), 7.81-7.86 (m, 4H). ^{13}C NMR (C_6D_6): δ 25.27, 67.57, 128.29, 131.09, 134.81, 135.48. MS: *m/e* 278 (M^++2, 5), 276 (M^+, 14), 261 (M^+-Me, 9), 241 (M^+-Cl, 6), 217 (M^+-*i*-PrO, 100), 198 (51), 181 (22) 157 (98). Anal. Calcd for $C_{15}H_{17}OSiCl$: C, 65.08; H, 6.19. Found: C, 65.49; H, 6.40.

(Methoxy)diphenylchlorosilane (9). To a mixture of diphenylchlorosilane (4.31 g, 19.7 mmol) and triethylamine (3.57 mL, 25.6 mmol) in hexane (80 mL) was added a mixture of methyl alcohol (1.04 mL, 25.6 mmol) in hexane (4 mL) over 5 min at -40 °C. The mixture was stirred at -40 °C for 3 h and warmed to the ambient temperature. The mixture was diluted with hexane (ca. 50 mL) and the salts were filtered wih suction. The filtrate was concentrated and the residue was distilled through a short path column (85-94 °C/0.40 mmHg) to give (methoxy)diphenylsilane (3.29 g, 78% yield) as colorless oil. A solution of the (methoxy)diphenylsilane (3.29 g, 15.3 mL) in carbon tetrachloride (5.0 mL) was added to a mixture of palladium chloride (17.3 mg, 9.76 x 10^{-2} mmol) and carbon tetrachloride (10 mL) at room temperature over 1 h. After stirring for 2 h, the mixture was concentrated, diluted with hexane (10 mL), and filtered. The filtrate was concentrated and the residue was distilled through a short path column (119-121 °C/1.50 mmHg) to give **9** (2.53 g, 97% purity by GLC, 67% yield) as colorless oil. ^{1}H NMR (C_6D_6): δ 3.46 (s, 3H), 7.12-7.17 (m, 6H), 7.76-7.80 (m, 4H). ^{13}C NMR (C_6D_6): δ 51.15, 128.38, 131.25, 134.76, 135.31. MS: *m/e* 250 (M^++2, 7), 248 (M^+, 14), 199 (21), 171 (19), 153 (100). Anal. Calcd for $C_{13}H_{13}OSiCl$: C, 62.76; H, 5.27. Found: C, 62.80; H, 5.42.

1-Chloro-1,1-diphenyl-2,2,2-trimethyldisilane (19). This compound was prepared in 83% overall yield by the similar method as described in the literature.[2] The spectral data were identical with the literature data.[13]

A Typical procedure for reduction of chlorosilane with LDMAN: Synthesis of [Bis(*tert*-butoxy)phenylsilyl]lithium (4) and Trapping as 1,1-Bis(*tert*-butoxy)-1-phenyl-2,2,2-trimethyldisilane (16). To a suspension of lithium granular (33 mg, 4.8 mg-atom) in THF (4.5 mL) was added 1-(dimethylamino)naphthalene (0.78 mL, 4.8 mmol) at room temperature. The green color appeared after 15 min and then the mixture was cooled to -50 °C. A solution of LDMAN was completely formed by vigorous stirring at the same temperature for 6 h. Bis(*t*-butoxy)phenylchlorosilane (**10**) (301 mg, 1.1 mmol) in THF (2.0 mL) was added over 9 min to the LDMAN solution at -50 °C. After stirring for 1 h, Me_3SiCl (0.66 mL, 5.2 mmol) was added to the silyllithium solution at -50 °C. After stirring for 10 min, the mixture was warmed to the ambient temperature. The volatile materials were evaporated under reduced pressure. The residue was diluted with hexane (10 mL), filtered, and evaporated. The residue was subjected to the reversed-phase column chromatography (30 mL) eluted with CH_3CN to separate the resulting 1-(dimethylamino)naphthalene ($R_f = 0.58$) to afford the crude **16** (555 mg) ($R_f = 0.40$) together with uncharacterized impurities. The yield was estimated by means of GLC analysis (93%): Eicosane was used as internal standard. The pure sample was obtained as colorless oil by preparative GLC. ^1H NMR (C_6D_6): δ 0.29 (s, 9H), 1.37 (s, 18H), 7.25-7.36 (m, 3H), 7.93-7.96 (m, 2H). ^{13}C NMR (C_6D_6): δ -1.02, 32.37, 73.34, 127.87, 129.35, 134.61, 140.97. MS: *m/e* 324 (M^+, 0.5), 309 (M^+-Me, 7), 251 (5), 211 (89), 139 (100). Anal. Calcd for $C_{17}H_{32}O_2Si_2$: C, 62.90; H, 9.94. Found: C, 62.67; H, 9.83.

1,2-Bis(*tert*-butoxy)-1,1,2,2-tetraphenyldisilane. The pure sample was obtained as colorless solid by recrystallization from hexane. mp 167.8-168.8 °C. ^1H NMR (C_6D_6): δ 1.31 (s, 18H), 7.19-7.20 (m, 12H), 7.87-7.92 (m, 8H). ^{13}C NMR (C_6D_6): δ 32.26, 74.52, 127.78, 129.62, 136.23, 138.22. MS: *m/e* 510 (M^+, 0.1), 495 (M^+-Me, 0.4), 437 (M^+-*t*-BuO, 0.7), 397 (100), 319 (65), 199 (99), 181 (21). Anal. Calcd for $C_{32}H_{38}O_2Si_2$: C, 75.24; H, 7.50. Found: C, 75.21; H, 7.54.

1-*tert*-Butoxy-1,1-diphenyl-2,2,2-trimethyldisilane (13). This compound[1] was obtained in 81% yield (GLC) by essentially the same method as described above.

1-Isopropoxy-1,1-diphenyl-2,2,2-trimethyldisilane (14). The pure sample was obtained as colorless oil by preparative GLC. ^{1}H NMR (C_6D_6): δ 0.28 (s, 9H), 1.16 (d, J = 6.3 Hz, 6H), 4.11 (septet, J = 6.3 Hz, 1H), 7.23-7.27 (m, 3H), 7.75-7.79 (m, 2H). ^{13}C NMR (C_6D_6): δ −1.22, 25.97, 66.83, 128.20, 129.71, 135.17, 137.85. MS: *m/e* 299 (M^+-Me, 0.4), 271 (M^+-*i*-Pr, 9), 255 (M^+-*i*-PrO, 6), 241 (M^+-Me_3Si, 23), 199 (100), 181 (25). Anal. Calcd for $C_{18}H_{26}OSi_2$: C, 68.73; H, 8.33. Found: C, 68.50; H, 8.16.

1-Methoxy-1,1-diphenyl-2,2,2-trimethyldisilane (15). The pure sample was obtained as colorless oil by preparative GLC. ^{1}H NMR (C_6D_6): 0.26 (s, 9H), 3.47 (s, 3H), 7.25-7.27 (m, 6H), 7.72-7.75 (m, 4H). δ ^{13}C NMR (C_6D_6): δ -1.40, 51.90, 128.31, 129.81, 134.99, 136.73. MS: *m/e* 286 (M^+, 2), 271 (M^+-Me, 100), 255 (M^+-MeO, 5), 183 (68). Anal. Calcd for $C_{16}H_{22}OSi_2$: C, 67.07; H, 7.74. Found: C, 67.10; H, 7.86.

1-(Diethylamino)-1,1-diphenyl-2,2,2-trimethyldisilane (17). This compound has been reported in Chapter 1.[2]

Synthesis of [Hydrodiphenylsilyl]lithium (6) and Trapping as 1-Hydro-1,1-diphenyl-2,2,2-trimethyldisilane (18). To a solution of LDMAN in THF (2.8 mL), which was prepared from lithium granular (20 mg, 2.8 mg-atom) and 1-(dimethylamino)naphthalene (0.47 mL, 2.8 mol), was added **12** (0.12 mL, 0.63 mmol) in THF (2.0 mL) at -50 °C over 5 min. After stirring for 1 h, Me_3SiCl (0.40 mL, 3.1 mmol) was added to the silyllithium solution at -50 °C. After stirring for 10 min, the mixture was warmed to the ambient temperature. After cooling to 0 °C, 1 M hydrochloric acid (10 mL) was poured into the reaction mixture, which was extracted with Et_2O (10 mL x 3). The combined organic layer

was washed with 1 M hydrochloric acid (10 mL), water (10 mL), and brine (10 mL), and dried over Na_2SO_4. The solution was concentrated in vacuo to yield the crude **18**. The yield was estimated by means of ^1H NMR analysis (40%): Mesitylene was used as internal standard. The pure sample was obtained as colorless oil by preparative GLC. The spectra data were identical with those of the literature.[13]

Attempted Synthesis of a (Disilanyl)lithium from 19: Formation of 2,2,3,3-Tetraphenyl-1,1,1,4,4,4-hexamethyltetrasilane (20). To a solution of LDMAN in THF (2.4 mL), which was prepared from lithium granular (17 mg, 2.5 mg-atom) and 1-(dimethylamino)naphthalene (0.40 mL, 2.5 mol), was added **19** (159 mg, 0.55 mmol) in THF (2.0 mL) at −78 °C over 10 min. After stirring for 15 min, Me_3SiCl (0.34 mL, 2.7 mmol) was added to the solution at −78 °C. After stirring for 10 min, the mixture was warmed to the ambient temperature. Usual workup as described above afforded the crude **20**. Recrystallization from hexane gave **20** as colorless solid (52% yield). mp 269−270 °C (in a sealed capillary under atmospheric pressure). Sublimination point: about 150 °C. ^1H NMR (C_6D_6): δ 0.14 (s, 18H), 7.17−7.20 (m, 12H), 7.71−7.75 (m, 8H). ^{13}C NMR (C_6D_6): δ −0.32, 128.22, 128.92, 136.14, 137.06. MS: *m/e* 510 (M^+, 16), 495 (M^+−Me, 5), 437 (M^+−Me_3Si, 12), 360 (89), 255 (Me_3Si-Ph_2Si^+, 87), 135 (100). Anal. Calcd for $C_{30}H_{38}Si_4$: C, 70.52; H, 7.50. Found: C, 70.34; H, 7.57.

Self-Condensation of [(Methoxy)diphenylsilyl]lithium (3): Formation of 1-Methoxy-1,1,2,2-tetraphenyl-3,3,3-trimethyltrisilane (22).

A solution of **3** in THF (4.5 mL), which was prepared at −78 °C from **9** (160 mg, 0.62 mmol), lithium granular (19 mg, 2.7 mg-atom), and 1-(dimethylamino)naphthalene (0.45 mL, 2.7 mol), was warmed to 0 °C. After 10 min, Me_3SiCl (3.0 mmol, 0.38 mL) was added to the solution. After stirring for 20 min, the reaction mixture was warmed to the ambient temperature. The reaction mixture was evaporated, diluted with hexane, and filtered. The filtrate was

concentrated to give a mixture of **22** and **15**. The yield of **15** was estimated by GLC analysis (9 %): Docosane was used as internal standard. The mixture was subjected to the reversed-phase column chromatography (30 mL) eluted with CH_3CN to separate the resulting 1-(dimethylamino)naphthalene ($R_f = 0.58$) to afford the crude **22** (115 mg, $R_f = 0.45$), followed by HPLC eluted with hexane/AcOEt (10/1) to yield **22** (42 mg, 29% yield) as colorless solid. mp 70.0-70.5 °C. ^1H NMR (C_6D_6): δ 0.26 (s, 9H), 3.49 (s, 3H), 7.15-7.20 (m, 12H), 7.68-7.72 (m, 4H), 7.71-7.81 (m,4H). ^{13}C NMR (C_6D_6): δ -0.55, 52.22, 128.18, 128.34, 128.92, 129.98, 135.26, 135.49, 136.59, 136.90. MS: *m/e* 468 (M^+, 27), 453 (M^+-Me, 45), 395 (M^+-Me_3Si, 8), 364 (96), 255 (Me_3Si-Ph_2Si^+, 20), 213 ($(MeO)Ph_2Si^+$, 100). Anal. Calcd for $C_{28}H_{32}OSi_3$: C, 71.74; H, 6.88. Found: C, 71.83; H, 6.88.

1-*tert*-Butoxy-1,1,2,2-tetraphenyl-3,3,3-trimethyltrisilane (21). This compound[1] was obtained in 48% yield as a mixture with **13** (25% GLC yield) by essentially the same method as described above. The yield was estimated from the relative intensity of ^1H NMR spectra to the disilane.

Reaction of 3 with *n*-Butyllithium: Formation of 1-*n*-Butyl-1,1-diphenyl-2,2,2-trimethyldisilane (23). To a solution of **3** in THF (5.0 mL), which was prepared from (methoxy)diphenylchlorosilane (0.66 mmol), lithium granular (3.0 mg-atom), and 1-(dimethylamino)naphthalene (3.0 mmol), was added *n*-BuLi in hexane (2.1 mL, 3.3 mmol) at -78 °C. After stirring at that temperature for 30 min, Me_3SiCl (0.87 mL, 6.9 mmol) was added to the solution. The reaction mixture was stirred at -78 °C for 20 min and warmed to the ambient temperature. A 1 M hydrochloric acid (10 mL) was poured into the reaction mixture and the mixture was extracted with Et_2O (10 mL x 3). The combined organic layer was washed with 1 M hydrochloric acid (10 mL x 2), water (10 mL), and brine (10 mL), and dried over $MgSO_4$. After filtration, the filtrate was concentrated and subjected to silica gel column chromatography eluted with hexane, followed by HPLC eluted with hexane

afforded **23** (128 mg, 62% yield). The spectra and analytical data have been reported in Chapter 6.[1]

Attempted Selfcondensation of 4. A solution of **4** in THF (5.0 mL), which was prepared at -50 °C from **10** (182 mg, 0.63 mmol), lithium granular (20 mg, 2.9 mg-atom), and 1-(dimethylamino)naphthalene (0.48 mL, 2.9 mmol), was warmed to 0 °C. After 2 h, Me_3SiCl (0.41 mL, 3.2 mmol) was added to the solution. After stirring for 10 min, the reaction mixture was warmed to the ambient temperature. The reaction mixture was evaporated, diluted with hexane, filtered, and condensed under reduced pressure. No self-condensation product (*t*-BuO)$_2$PhSi(*t*-BuO)PhSi-$SiMe_3$ was detected in the residue by ^{1}H NMR analysis. The residue was subjected to the reversed-phase column chromatography (20 mL) eluted with CH_3CN to separate the resulting 1-(dimethylamino)naphthalene (R_f = 0.58) to afford the crude **16** (197 mg) (R_f = 0.40) together with uncharacterized impurities. The yield was estimated by means of GLC analysis (76%): Eicosane was used as internal standard.

Attempted Reaction of 4 with *n*-Butyllithium. A solution of **4** in THF (3.3 mL), which was prepared at -50 °C from **10** (151 mg, 0.53 mmol), lithium granular (16 mg, 2.3 mg-atom), and 1-(dimethylamino)naphthalene (0.38 mL, 2.3 mmol), was added to a solution of *n*-BuLi in hexane (2.5 mL, 4.2 mmol) and tetramethylethylenediamine (0.64 mL, 4.2 mmol) in THF (2.0 mL) at 0 °C over 2 min via a Teflon tube. After stirring at 0 °C for 2 h, Me_3SiCl (0.91 mL, 7.2 mmol) was added to the solution. The reaction mixture was stirred at 0 °C for 20 min and warmed to the ambient temperature. The reaction mixture was evaporated, diluted with hexane, filtered, and condensed under reduced pressure. Butylation products (*t*-BuO)(*n*-Bu)PhSi-$SiMe_3$ and (*n*-Bu)$_2$PhSi-$SiMe_3$ were not detected in the residue by ^{1}H NMR analysis. The residue was subjected to the reversed-phase column chromatography (20 mL) eluted with CH_3CN to separate the resulting 1-(dimethylamino)naphthalene (R_f = 0.58) to afford the crude **16** (215 mg) (R_f =

0.40) together with uncharacterized impurities. The yield was estimated by means of GLC analysis (73%): Eicosane was used as internal standard.

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Chapter 8

Contrasting Reactivities of Monoalkoxy- and Dialkoxyphenylchlorosilanes toward Lithium Metal: Selective Formation of 2-(Alkoxy)disilanyllithium vs Dialkoxymonosilyllithium

Abstract: Reaction of di(alkoxy)chlorosilane gives the (dialkoxysilyl)lithium selectively. In contrast, reaction of mono(alkoxy)chlorosilanes with lithium metal at 0 °C gives β-(alkoxy)disilanyllithiums selectively via immediate self-condensation of the resulting (alkoxy)silyllithiums. The [2-(alkoxy)disilanyl]lithiums undergo coupling with chlorosilane and 1,4-addition to an α,β-unsaturated ester.

Introduction

Silyl anions,[1] especially functionalized silyl anions[2] and oligosilanyl anions,[3] are useful reagents for constructing silicon-silicon skeletons of oligosilanes and polysilanes and for introducing various silyl units to organic compounds.[2c,4] In view of only a few number of such species reported so far, development of new methodologies has been highly awaited. In particular, oligosilanyl anions are not so readily obtained, because preparation of the precursors, linear or cyclic oligosilanes, is often tedious.[5] Described herein is the most convenient one-step synthesis of 2-[(alkoxy)disilanyl]lithiums and a dialkoxy-monosilyllithium from readily available monosilanes, with a special emphasis on the contrasting reactivities of the precursors, monoalkoxy- and dialkoxy-chlorosilanes.

The author has recently prepared (alkoxysilyl)lithiums by a tin-lithium exchange reaction of (alkoxysilyl)stannanes with *n*-butyllithium[2a] and by reduction of (alkoxy)chlorosilanes with lithium 1-(dimethylamino)naphthalenide[2b] at low temperatures.[6] The (monoalkoxysilyl)lithiums behave as lithium (alkoxy)silylenoids, which undergo bimolecular self-condensation at 0 °C by nucleophilic substitution of the alkoxy group by another molecule of silyllithium, to

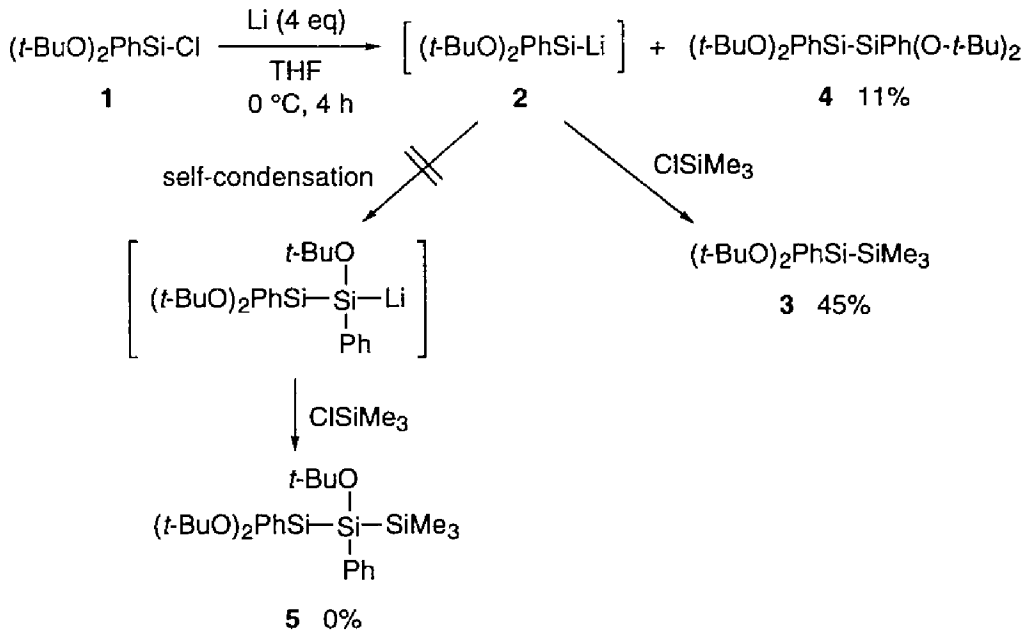
yield [2-(alkoxy)disilanyl]lithiums. In contrast, the (dialkoxysilyl)lithium show little silylenoid nature. These findings prompted the author to investigate a direct reaction of (alkoxy)chlorosilanes with lithium metal.

Results and Discussion

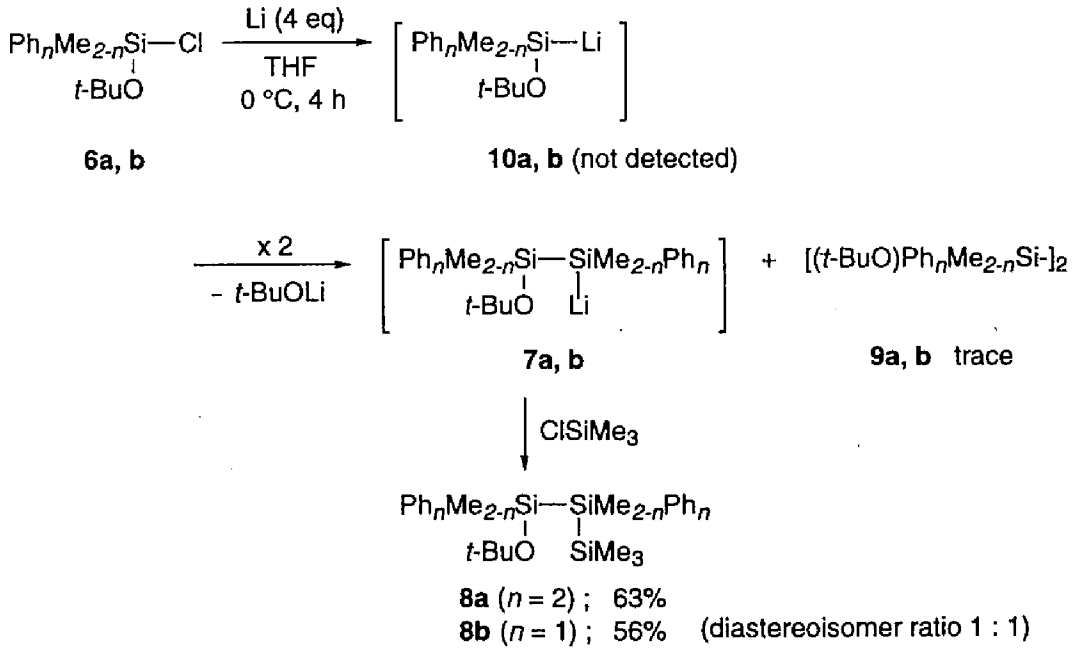
The author first examined a reaction of (dialkoxy)chlorosilane **1** (Scheme 1). Thus, **1** was stirred with an excess amount of lithium granular[7] (4 equiv) in THF at 0 °C for 4 h followed by trapping with Me_3SiCl to give 1,1-dialkoxy-1-phenyl-trimethyldisilane **3** in 45% yield, together with a homocoupling product **4** in 11% yield.[8] The result clearly indicates the formation of (dialkoxysilyl)lithium **2** which is, as expected from the previous results, stable at 0 °C and gives no self-condensation product **5** at all. This is the first example for the synthesis of (alkoxysilyl)lithium by the direct reaction of (alkoxy)chlorosilane with lithium metal. In the ^{29}Si NMR spectrum, **2** resonates at δ 41.8, being highly downfield compared to that of **1** (δ 10.0).[2b]

In contrast, reaction of (monoalkoxy)chlorosilanes **6** with lithium granular[7] (4 equiv) in THF at 0 °C afforded [2-(alkoxy)disilanyl]lithiums **7**, which were trapped after 4 h by Me_3SiCl to give the corresponding (alkoxy)trisilanes **8** in about 60% yields, together with a trace amount of homocoupling product **9** (Scheme 2). It is likely that the silylenoids [alkoxysilyl]lithiums **10** are generated in the first step and they undergo bimolecular self-condensation immediately, as reported recently.[2a] Not only the diphenyl **6a** but also the phenylmethyl **6b** derivative afforded comparable results. This is the most convenient, one step synthesis of disilanyllithiums **7** from readily available monosilanes.

Scheme 1

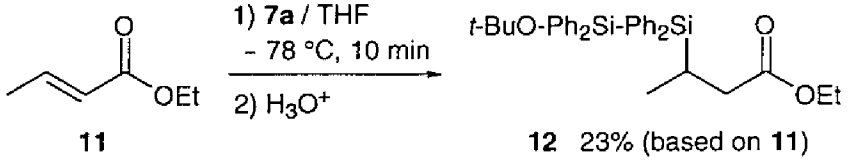


Scheme 2



The ^{29}Si NMR spectroscopy showed two signals at δ -43.7 (Li-Si) and -2.3 (O-Si) for **7a** and two sets of signals, at δ -64.5, -62.7 (Li-Si) and 8.1, 9.0 (O-Si) for **7b**, which are attributed to the diastereoisomers.

The disilanyllithium **7a** underwent 1,4-addition to an α,β-unsaturated ester **11** to give β-disilanylated ester **12** in 23% yield (eq. 1).[4]



11 **12** 23% (based on **11**) (1)

The stability of the [2-(alkoxy)disilanyl]lithiums **7** is worthy of note. No further elongation reaction of **7** was observed, probably due to lack of the activation of Si-O bond by lithium atom unlike in the silylenoids **10**. However, **7** slowly decomposed in THF at 0 °C; for example, after 24 h, the yields of the trapped products substantially decreased, **8a** (31% yield) and **8b** (16% yield), respectively. No characterizable decomposition products has been isolated so far.

The author has developed a new method for preparation of [2-(alkoxy)disilanyl]lithiums via lithium (alkoxy)silylenoids, as well as a (dialkoxysilyl)lithium. The silylenoids have thus potential utility for preparation of new reagents in addition to elucidation of the mechanism of polysilane synthesis.[9] Further studies on functionalized monosilyl- and disilanyllithiums are currently in progress, especially for clarification of the origin of the reactivity difference between monoalkoxy- and (dialkoxysilyl)lithiums and decomposition mode of [2-(alkoxy)disilanyl]lithiums.

Experimental Section

General Remarks. ^{1}H (270 MHz), ^{13}C (67.94 MHz), and ^{29}Si (53.67 MHz) NMR spectra were recorded on a JEOL EX-270 spectrometer. ^{1}H and ^{13}C chemical shifts are referenced to internal benzene-d_6 (^{1}H δ 7.200 ppm and ^{13}C δ 128.00 ppm) or $CDCl_3$ (^{13}C δ 77.00 ppm). ^{29}Si chemical shifts are referenced to external

tetramethylsilane (0 ppm). The ^{29}Si NMR spectra were observed in an unlocked mode at 0 °C. Although the spectrometer was unlocked during the acquisition, the field was stable and no significant field shift was observed. For NMR measurements, the silyllithium **2** and disilanyllithium **7** were prepared in THF as described in the experimental procedures and the resulting solution were transfered to an NMR sample tube via a Teflon tube under an argon atmosphere. Mass spectra were measured at 70 eV on a JEOL JMS-DX300 mass spectrometer equipped with a JMA-3500 data processing system. Melting points were measured with a Yanaco-MP-S3 apparatus and were uncorrected. The elemental analyses were performed at the Microanalysis Division of Institute for Chemical Research, Kyoto University: Analytical samples were purified by preparative GLC, preparative HPLC, or recrystallization. Analytical and preparative GLC were performed on a Shimadzu GC-4B gas chromatography, equipped with a 3-m or 1-m column packed with 30% Silicone DC550 on Celite 545. Column chromatography was performed by using Kieselgel 60 (70–230 mesh) (Merck). Thin layer chromatography (TLC) was performed on plates of silica gel 60F-254 (Merck).

(*tert*-Butoxy)diphenylchlorosilane and bis(*tert*-butoxy)phenylchlorosilane were prepared by the same method as described in the literature.[2b] Phenylmethyldichlorosilane was distilled under reduced pressure before use. Trimethylchlorosilane was treated with sodium cuts under nitrogen to remove the dissolving HCl and the supernatant was used. Triethylamine was distilled under nitrogen from calcium hydride. *tert*-Butyl alcohol was distilled from calcium hydride. 4-(Dimethylamino)pyridine was commercially available and used without further purification. Lithium granular was purchased from Chemetall Gesellshaft. THF was distilled under nitrogen from sodium benzophenone ketyl. All reactions were carried out under an argon atmosphere.

Synthesis of [Bis(*tert*-butoxy)phenylsilyl]lithium (2) and Trapping as 1,1-Bis(*tert*-butoxy)-1-phenyl-2,2,2-trimethyldisilane (3). To a suspension of lithium granular (32 mg, 4.6 mg-atom) in THF (1.0 mL) was added bis(*tert*-butoxy)phenylchlorosilane (**1**) (296 mg, 1.03 mmol) at room

temperature. The lithium surface turned orange after 40 min and the mixture was cooled to 0 °C. After being stirred for 4 h, the resulting dark red solution of **2** was added via a Teflon tube to a solution of trimethylchlorosiane (0.14 mL, 1.1 mmol) in THF (1.0 mL) at 0 °C. The mixture was stirred at 0 °C for 20 min and warmed to the ambient temperature. The solvent was evaporated. The residue was diluted with hexane (10 mL), filtered, and concentrated. The residue was distilled bulb-to-bulb (105–125 °C/0.35 mmHg, bath temperature) to give **3** (149 mg, 45% yield) as colorless liquid. The spectral data were identical with the data reported described in Chapter 7.[2b] The residue was further distilled bulb-to-bulb (140–170 °C/0.3 mmHg, bath temperature) to give crude **4** (38 mg, 51% purity by GLC, approximately 11% yield).

1,1,2,2-Tetrakis(*tert*-butoxy)-1,2-diphenyldisilane (4). To a suspension of lithium granular (14 mg, 2.0 mg-atom) in THF (2.0 mL) was added **1** (557 mg, 1.94 mmol) at room temperature. The ultrasonication was performed until the lithium surface turned orange (about for 5 min) and the mixture was stirred at room temperature. After being stirred for 1 day, the solvent was evaporated. The residue was diluted with hexane (10 mL), filtered, and concentrated to give crude **4** as white solid. Recrystallization from hexane at 0 °C afforded pure **4** (294 mg, 60% yield) as colorless crystal: mp 215–216 °C (in a capillary under atmospheric pressure). Sublimination point: about 160 °C. ^{1}H NMR (C_6D_6): δ 1.36 (s, 36H), 7.25–7.39 (m, H), 8.22–8.25 (m, 4H). ^{13}C NMR (C_6D_6): δ 32.30, 73.99, 127.52, 129.49, 135.76, 140.63. MS: *m/e* 487 (M^+–Me, 0.5), 429 (M^+–*t*-BuO, 0.7), 277 (55), 199 (4), 139 (100). Anal. Calcd for $C_{28}H_{46}O_4Si_2$: C, 66.88; H, 9.22. Found: C, 66.70; H, 9.30.

(*tert*-Butoxy)phenylmethylchlorosilane (6b). This compound was prepared from phenylmethydilchlorosilane and *tert*-butyl alcohol in 68% yield by essentially the same method as described in Chapter 7:[2b] bp 61–64 °C/1.0 mmHg. ^{1}H NMR (C_6D_6): δ 0.62 (s, 3H), 1.28 (s, 9H), 7.20–7.22 (m, 3H), 7.77–7.81 (m, 2H). ^{13}C NMR (C_6D_6): δ 3.96, 31.65, 75.71, 128.18, 130.59, 133.73, 136.64.

MS: *m/e* 230 (M^++2, 3), 228 (M^+, 7), 215 (M^++2-Me, 41) 213 (M^+-Me, 100), 157 (M^++2-*t*-BuO, 52) 155 (M^+-*t*-BuO, 68). Anal. Calcd for $C_{11}H_{17}OSiCl$: C, 57.75; H, 7.49. Found: C, 57.87; H, 7.09.

Synthesis of (2-*tert*-Butoxy-1,1,2,2-tetraphenyldisilanyl)lithium (7a) and Trapping as 1-*tert*-Butoxy-1,1,2,2-tetraphenyl-3,3,3-trimethyltrisilane (8a). To a suspension of lithium granular (29 mg, 4.2 mg-atom) in THF (1.0 mL) was added **6a** (309 mg, 1.06 mmol) at room temperature. The lithium surface turned orange after 20 min and the mixture was cooled to 0 °C. After being stirred for 4 h, the resulting dark red solution of **7a** was added via a Teflon tube to a solution of trimethylchlorosiane (0.15 mL, 1.2 mmol) in THF (1.0 mL) at 0 °C. The mixture was stirred at 0 °C for 20 min and warmed to the ambient temperature. A 5% aq. solution of NH_4Cl (10 mL) was then poured into the mixture. The mixture was extracted with Et_2O (10 mL x 3). The combined organic layer was washed with water (10 mL) and brine (10 mL), and dried over $MgSO_4$, and concentrated in vacuo. The white solid obtained was subjected to the column chromatography on silica gel eluted with hexane/AcOEt (60/1) to afford the crude **8a** (236 mg, R_f = 0.23) together with small amounts of impurities. The crude solid product was triturated with hexane (1 mL x 2) at 0 °C followed by filtration to give pure **8a** (170 mg, 63%) as white solid. The spectral data were identical with the data described in Chapter 6.[2]

Synthesis of (2-*tert*-Butoxy-1,2-diphenyl-1,2-dimethyldisilanyl)-lithium (7b) and trapping as 1-*tert*-Butoxy-1,2-diphenyl-1,2-dimethyl-3,3,3-trimethyltrisilane (8b).

To a suspension of lithium granular (31 mg, 4.4 mg-atom) in THF (1.0 mL) was added **6b** (236 mg, 1.03 mmol) at room temperature. The lithium surface turned orange after 10 min and the mixture was cooled to 0 °C. After being stirred for 4 h, the resulting dark red solution of **7b** was added via a Teflon tube to a solution of trimethylchlorosiane (0.14 mL, 1.1 mmol) in THF (1.0 mL) at 0 °C. The mixture was stirred at 0 °C for 20 min and warmed to the ambient temperature. The

solvent was evaporated. The residue was diluted with hexane (10 mL), filtered, and concentrated. The colorless liquid obtained was subjected to the column chromatography on silica gel eluted with hexane to afford **8b** (111 mg, R_f = 0.20, a 1:1 mixture of diastereoisomers) as colorless oil. ^{1}H NMR (C_6D_6): δ 0.22 (s, 9H), 0.25 (s, 9H), 0.45 (s, 3H), 0.49 (s, 3H), 0.64 (s, 3H), 0.70 (s, 3H), 1.19 (s, 9H), 1.21 (s, 9H), 7.23-7.28 (m, 6H), 7.59-7.67 (m, 4H). ^{13}C NMR ($CDCl_3$): δ -9.04, -8.73, -1.26 (2C) 1.21, 1.33, 32.20 (2C), 73.86, 73.98, 127.42, 127.48 (2C), 127.55; 127.64 (2C), 127.67, 128.72, 128.75, 133.60, 133.69, 134.84, 137.25, 137.45, 140.97, 141.19. MS: *m/e* 386 (M^+, 0.4), 371 (M^+-Me, 1), 329 (M^+-*t*-Bu, 100), 313 (M^+-$SiMe_3$, 7), 193 (18). Anal. Calcd for $C_{21}H_{34}OSi_3$: C, 65.22; H, 8.86. Found: C, 64.86; H, 8.90.

Reaction of 7a with Ethyl crotonate: Synthesis of Ethyl 3-(2'-*tert*-butoxy-1',1',2',2'-tetraphenyldisilanyl)butanoate (12). A solution of **7a**, which was prepared from **6a** (277 mg, 0.952 mmol) and lithium granular (28 mg, 4.0 mmol) in THF (1.0 mL), was added over 1 min to a solution of ethyl crotonate (**11**) in THF (1.0 mL) at -78 °C and stirred for 10 min. A 5% aq. solution of NH_4Cl (5 mL) was poured into the mixture at -78 °C. After being warmed to the ambient temperature, the mixture was extracted with Et_2O (10 mL x 3). The combined organic layer was washed with 5% aq. solution of NH_4Cl (10 mL x 1), water (10 mL x 1), brine (10 mL x 1), dried over $MgSO_4$, and concentrated in vacuo. The residue was subjected to the column chromatography on silica gel eluted with hexane/AcOEt (20/1) to give crude **12** (124 mg, R_f = 0.20), followed by HPLC with hexane/AcOEt (7/1) to pure **12** (59 mg, 23% yield) as colorless oil: ^{1}H NMR (C_6D_6): δ 0.96 (t, J = 7.2 Hz, 3H), 1.27 (s, 9H), 1.36 (d, J = 7.0 Hz, 3H), 2.28 (dd, J = 14.9 and 12.2 Hz, 1H), 2.30-2.48 (m, 1H), 3.15 (dd, J = 14.9 and 1.6 Hz, 1H), 3.98 (q, J = 7.2 Hz, 2H), 7.12-7.20 (m, 12H), 7.66-7.83 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 14.25, 14.76, 15.11, 32.04, 37.25, 60.00, 75.47, 127.57 (4C), 128.88, 128.95, 129.38 (2C), 133.73, 133.78, 135.54, 135.58, 136.33, 136.39, 136.73, 136.77. MS: *m/e* 523 (M^+-Et, 0.4), 507 (M^+-EtO, 0.7), 479 (M^+-*t*-

BuO, 0.5), 451 (1), 297 (M^+-(*t*-BuO)Ph_2Si, 100). Anal. Calcd for $C_{34}H_{40}O_3Si_2$: C, 73.87; H, 7.29. Found: C, 73.55; H, 7.40.

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(7) Using lithium dispersion gave the lower yields of **3** and **8**, respectively, together with uncharacterized by-products.

(8) When only one equimolar amount of lithium metal used at room temperature, the sterically crowded homocoupling product, tetrakis(*tert*-butoxy)diphenyldisilane **4**, was obtained selectively in 60% yield (see Experimental Section).

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Chapter 9

Sila-Wittig Rearrangement

Abstract: (Allyloxysilyl)lithiums undergo [2,3]Wittig-type rearrangement smoothly to form lithium allylsilanolates. A crossover reaction supports the intramolecular rearrangement mechanism. This is the first example of sila-Wittig rearrangement.

Introduction

[2,3]Sigmatropic rearrangement, which involves an oxycarbanion as the migrating terminus, is well known as the [2,3]Wittig rearrangement.[1,2] The author has found the first example of the sila-Wittig rearrangement, anionic allyl group migration from oxygen to silicon, analogous to the [2,3]Wittig rearrangement (Scheme 1).[3] Initially, the author expected that (*tert*-butoxysilyl)lithium **1**/12-crown-4, which was described as a silyl anion system in chapter 6, might undergo migration of the *tert*-butyl group from oxygen to silicon.[4] No rearrangement, however, occurred at all, possibly due to a low migratory aptitude of the *tert*-butyl group (Scheme 2).[5] Then the attention was turned to (allyloxysilyl)lithiums in view of a high migratory aptitude of the allyl group in [2,3]Wittig rearrangement.

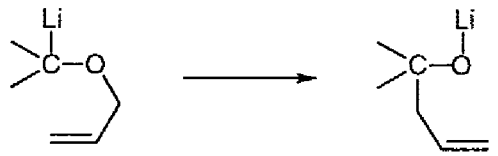
Results and Discussion

(Allyloxysilyl)stannane **2**, which has an allyloxy and a *tert*-alkoxy moiety on the same group, was treated with 2 equiv of *n*-butyllithium[6] in THF at −78 °C for 3 h followed by stirring at room temperature for 2 h to form the rearrangement product, lithium allylsilanolate **3**, which was trapped by Me_3SiCl to afford the corresponding allyldisiloxane **4** in 57% yield (Scheme 3).[6] By using large excess amounts of *n*-butyllithium (4 equiv), the yield of **4** was raised to 68% yield. The formation of the intermediate (allyloxysilyl)lithium **5** has been confirmed by trapping

with Me_3SiCl at −78 °C to afford (allyloxy)disilane **6** in 51% yield.[7] At this time, the rearrangement product **4** was also obtained in 21% yield. This result indicates that the allyl group has migrated completely from oxygen to silicon in the silyllithium **5** during warming-up to room temperature. No [1,2]rearrangement products were observed at all.

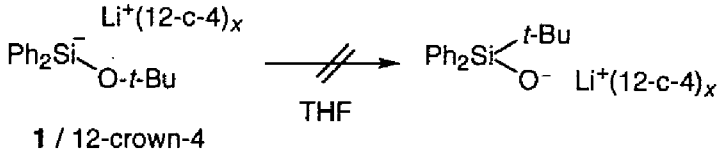
Scheme 1

Wittig Rearrangement



Sila-Wittig Rearrangement

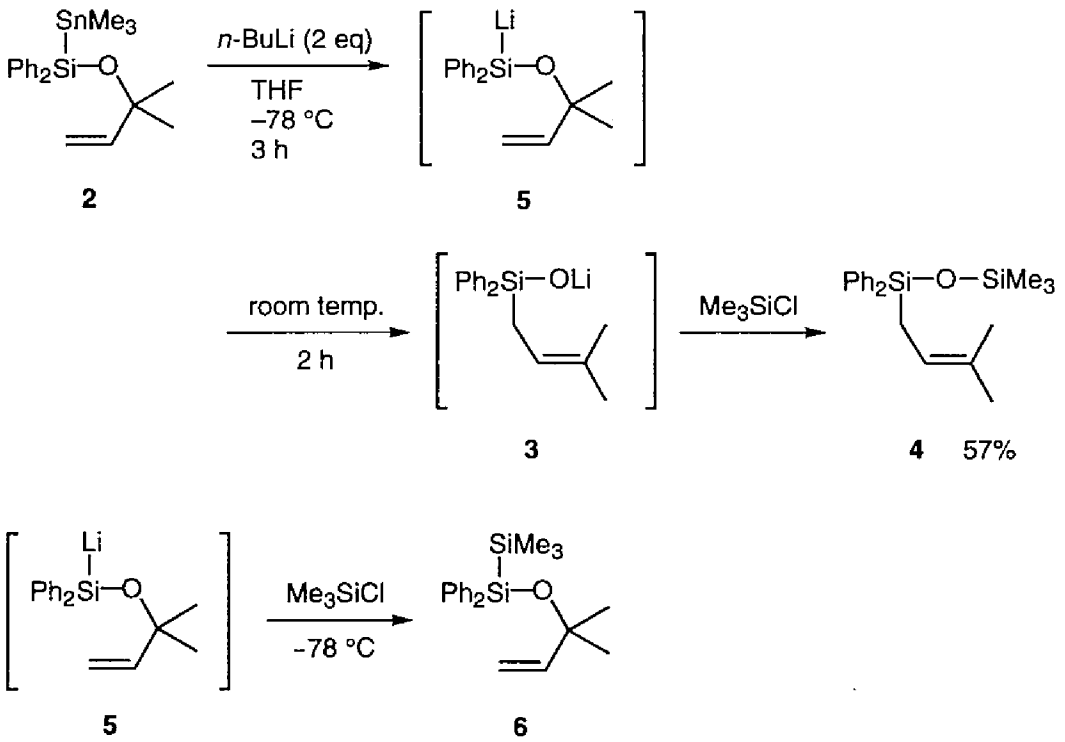
Scheme 2



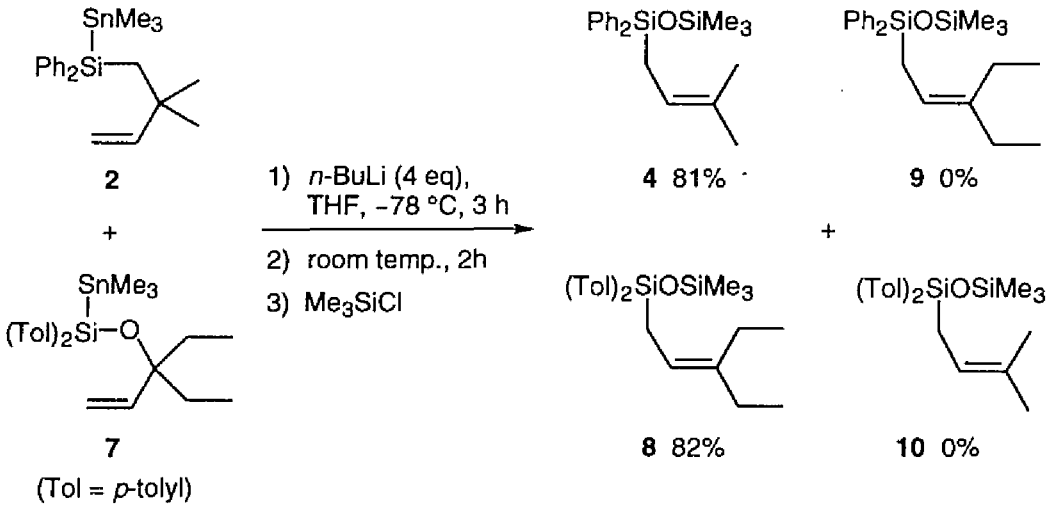
In the presence of 12-crown-4, **5** rearranged completely into **3** even at −78 °C: The stannane **2** was treated with 2 equiv of *n*-butyllithium in the presence of 12-crown-4 in THF at −78 °C for 3 h followed by being trapped by Me_3SiCl to afford no amount of **6** but **4** in 37% yield, together with recovered **2** in 33% yield.[8] This finding may be explained in terms of an increase in the anionic character of **5**, as reported in the Wittig rearrangement.[2]

The intramolecularity of the rearrangement has also been confirmed by the following crossover experiment (Scheme 4). An equimolar mixture of two kinds of (allyloxysilyl)stannane **2** and **7** was treated with *n*-butyllithium (4 equiv) under the same conditions as above to give only the intramolecular rearrangement products **4** and **8** in 81% and 82% yields, respectively. No cross-over products **9** and **10** were detected at all. It may be noted that the (allyloxysilyl)lithium species such as **5** in these transformations never underwent self-condensation, making a sharp contrast to the behavior of the (*tert*-butoxysilyl)lithium **1**.[4,9] The results imply that the intramolecular rearrangement of the (allyloxysilyl)lithiums proceed much faster than the bimolecular self-condensation.

Scheme 3

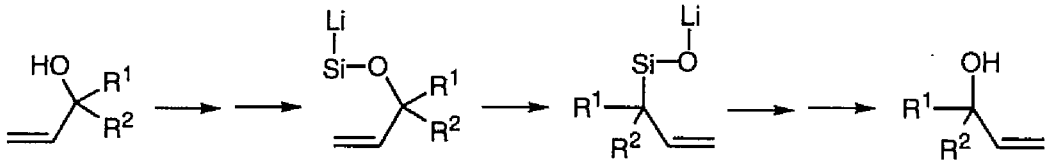


Scheme 4



The sila-Wittig rearrangement shows utility for preparation of sila-functionalized allylsilanes, which are expected to be synthetically useful. One example is their conversion into the corresponding allyl alcohols by H_2O_2 oxidation.[10] Thus, this may offer a novel 1,3-skeletal transformation of allyl alcohols (Scheme 5).

Scheme 5



Experimental Section

General Remarks. ^{1}H (200 MHz) and ^{13}C (50.29 MHz) NMR spectra were recorded on a Varian VXR-200 spectrometer or ^{1}H (270 MHz) and ^{13}C (67.94 MHz) NMR spectra were recorded on a JEOL EX-270 spectrometer. ^{1}H and ^{13}C chemical shifts are referenced to internal benzene-d_6 (^{1}H δ 7.200 ppm and ^{13}C δ 128.00 ppm) or $CDCl_3$ (^{13}C δ 77.00 ppm). Mass spectra were measured at 70 eV on a JEOL JMS-DX300 mass spectrometer equipped with a JMA-3500 data processing system. Melting points were measured with a Yanaco-MP-S3 apparatus and were uncorrected. The elemental analyses were performed at the Microanalysis Division of Institute for Chemical Research, Kyoto University: Analytical samples were purified by preparative GLC, preparative HPLC, or recycling reversed-phase liquid column chromatogrphy. Analytical and preparative GLC were performed on a Shimadzu GC-4B gas chromatography, equipped with a 3-m or 1-m column packed with 30% Silicone DC550 on Celite 545. Recycling reversed-phase liquid chromatogrphy was performed with JAI LC-908 equipped with JAIGEL-ODS S-343-15 and P-15 columns. Revesed-phase column chromatography was performed by using Wakogel LP-40C18 (20–40 μm) (Wako Pure Chemical Industries). Reversed-phase thin layer chromatography was performed on plates of RP-18 F_{254s} (Merck). Column chromatography was performed by using Kieselgel 60 (70–230 mesh) (Merck). Thin layer chromatography was performed on plates of silica gel 60F-254 (Merck).

Trimethylchlorostannane was prepared by disproportionation between tetramethylstannane and dimethyldichlorostannane:[11] the last was kindly donated from the Nitto Kasei Co. Trimethylchlorosilane was treated with sodium cuts under nitrogen to remove the dissolving HCl and the supernatant was used. Silicon tetrachloride was purchased from Wako Pure Chemical Industries and distilled before use. *n*-Butyllithium in hexane and lithium granular were purchased from Wako Pure Chemical Industries and Chemetall Gesellshaft, respectively. THF was distilled under nitrogen from sodium benzophenone ketyl. 12-crown-4 was

purchased from Aldrich and dried over Molecular Sieves 3A before use. All reactions were carried out under an argon atmosphere.

(2-Methyl-3-buten-2-oxy)diphenylchlorosilane. This compound was prepared from diphenyldichlorosilane and 2-methyl-3-buten-2-ol in 83% yield by essentially the same method as described in the literature.[4,9] bp 136–140 °C/1.0 mmHg. ^{1}H NMR (C_6D_6): δ 1.38 (s, 6H), 4.90 (dd, J = 10.7 and 1.4 Hz, 1H), 5.24 (dd, J = 17.2 and 1.4 Hz, 1H), 5.96 (dd, J = 10.7 and 17.2 Hz, 1H), 7.15–7.19 (m, 3H), 7.84–7.89 (m, 2H).

[(2-Methyl-3-buten-2-oxy)diphenylsilyl]trimethylstannane (2). (1) Trimethylstannyllithium was prepared by the literature method[12] from trimethylstannyl chloride (2.36 g, 11.9 mmol) with lithium granular (322 mg, 47.4 mg-atom) in THF (17 mL). The resulting solution was used for the next step without titration after removal of the unreacted lithium. (2) To a solution of (2-methyl-3-buten-2-oxy)diphenylchlorosilane (3.46 g, 11.4 mmol) in THF (10 mL) was added the THF solution of trimethylstannyllithium over 10 min at 0 °C and the mixture was stirred at 0 °C for 1 h and at room temperature for 14 h. The reaction mixture was evaporated, diluted with hexane (20 mL), and filtered. The filtrate was concentrated and the residue was distilled bulb-to-bulb to give **2** (3.76 g, 74% yield) as colorless oil. bp 140–155 °C/1.1 mmHg (bath temperature). ^{1}H NMR (C_6D_6): δ 0.32 (s, 9H), 1.34 (s, 6H), 4.92 (dd, J = 10.6 and 1.4 Hz, 1H), 5.21 (dd, J = 17.3 and 1.4 Hz, 1H), 5.97 (dd, 17.3 and 10.6 Hz, 1H), 7.23–7.25 (m, 3H), 7.75–7.80 (m, 2H). ^{13}C NMR (C_6D_6): δ −9.69, 30.20, 75.35, 111.98, 128.30, 129.78, 134.69, 139.67, 146.04. MS: *m/e* 432 (M^+, 0.9), 430 (0.7), 417 (M^+–Me, 10), 415 (8), 413 (5), 363 (55), 361 (40), 359 (23), 267 (100), 199 (291). Anal. Calcd for $C_{20}H_{28}OSiSn$: C, 55.70; H, 6.54. Found: C, 55.63; H, 6.54.

Reaction of 2 with *n*-Butyllithium and Subsequent Rearrangement: Synthesis of 1-(3'-Methyl-2'-butenyl)-1,1-diphenyl-3,3,3-trimethyldisiloxane (4). To a solution of **2** (431 mg, 1.00 mmol) in

THF (2.0 mL) was added dropwise over 1 min *n*-butyllithium in hexane (1.18 mL, 2.00 mmol) at −78 °C and the solution was stirred for 3 h. The solution was warmed to the ambient temperature and stirred for 2 h. To the solution was added trimethylchlorosilane (0.278 mL, 2.20 mmol). After being stirred for 15 min, the reaction mixture was diluted with hexane (10 mL) and filtered. The filtrate was concentrated and the residue was subjected to column chromatography on silica gel (30 mL) eluted with hexane to give **4** (194 mg, $R_f = 0.33$) in 57% yield as colorless oil. ^{1}H NMR (C_6D_6): δ 0.18 (s, 9H), 1.48 (s, 3H), 1.67 (d, J = 1.0 Hz, 3H), 2.13 (d, J = 8.2 Hz, 2H), 5.40–5.51 (m, 1H), 7.23–7.27 (m, 6H), 7.71–7.75 (m, 4H). ^{13}C NMR (C_6D_6): δ 2.03, 17.76, 18.30, 25.90, 118.58, 130.54, 128.00, 129.85, 134.63, 137.35. MS: *m/e* 340 (M^+, 4), 325 (M^+−Me, 2), 271 (100), 255 (9), 193 (39). Anal. Calcd for $C_{20}H_{28}OSi_2$: C, 70.53; H, 8.29. Found: C, 70.28; H, 8.26.

Reaction of 2 with *n*-Butyllithium: Synthesis of [(2-Methyl-3-buten-2-oxy)diphenylsilyl]lithium (5) and Trapping as 1-(2'-Methyl-3'-buten-2'-oxy)-1,1-diphenyl-2,2,2-trimethyldisilane (6). To a solution of **2** (227 mg, 0.526 mmol) in THF (2.0 mL) was added dropwise over 1 min *n*-butyllithium in hexane (0.64 mL, 1.1 mmol) at −78 °C and the solution was stirred for 3 h. To the solution was added trimethylchlorosilane (0.15 mL, 1.2 mmol) at −78 °C. After being stirred for 30 min, the solution was warmed to the ambient temperature. The reaction mixture was evaporated, diluted with hexane (20 mL), and filtered. The filtrate was concentrated and the residue was subjected to column chromatography on silica gel (20 mL) eluted with hexane/AcOEt (30/1) to give a mixture (148 mg, $R_f = 0.55$) of **4** (21% yield), **6** (51% yield), and 1,2-di(2'-methyl-3'-buten-2'-oxy)-1,1,2,2-tetraphenyldisilane (13% yield). The yields were estimated by ^{1}H NMR analysis. **1-(2'-Methyl-3'-buten-2'-oxy)-1,1-diphenyl-2,2,2-trimethyldisilane (6):** The pure sample was obtained by an alternative synthesis from 1-chloro-1,1-diphenyl-2,2,2-trimethyldisilane and 2-methyl-3-buten-2-ol by the similar method as described in the literature[4,9] and purified by column chromatography on silica gel eluted with hexane/AcOEt (R_f = 0.28) (47% yield). ^{1}H NMR (C_6D_6): δ 0.27 (s, 9H), 1.31 (s, 6H), 4.91 (dd, J =

10.6 and 1.6 Hz, 1H), 5.25 (dd, J = 17.2 and 1.6 Hz, 1H), 5.98 (dd, 17.2 and 10.6 Hz, 1H), 7.23-7.27 (m, 6H), 7.77-7.82 (m, 4H). ^{13}C NMR ($CDCl_3$): δ -1.20, 30.26, 74.75, 110.98, 127.60, 129.09, 134.91, 138.65, 146.51. MS: *m/e* 340 (M^+, 0.3), 325 (M^+-Me, 4), 272 (100), 271 (115), 267 (38), 255 (37), 199 (101), 193 (151). **1,2-Di(2'-methyl-3'-buten-2'-oxy)-1,1,2,2-tetraphenyldisilane:** The pure sample was obtained as colorless crystal by recrystallization from hexane. mp 166-167 °C. ^1H NMR (C_6D_6): δ 1.35 (s, 12H), 4.88 (dd, J = 10.7 and 1.6 Hz, 1H), 5.19 (dd, J = 17.3 and 1.6 Hz, 1H), 6.03 (dd, 17.3 and 10.7 Hz, 1H), 7.19-7.20 (m, 12H), 7.88-7.92 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 30.08, 75.92, 110.80, 127.28, 129.16, 135.89, 137.38, 146.38. MS: *m/e* 534 (M^+, 0.1), 519 (M^+-Me, 1), 465 (0.3), 397 (101), 319 (100), 267 (53), 199 (100). Anal. Calcd for $C_{34}H_{38}O_2Si_2$: C, 76.35; H, 7.16. Found: C, 76.48; H, 7.00.

Reaction of 2 with *n*-Butyllithium in the Presence of 12-Crown-4. To a solution of **2** (100 mg, 0.232 mmol) and 12-crown-4 (0.075 mL, 0.46 mmol) in THF (1.0 mL) was added dropwise over 1 min *n*-butyllithium in hexane (0.28 mL, 0.46 mmol) at -78 °C and the solution was stirred for 3 h. To the solution was added trimethylchlorosilane (0.065 mL, 0.51 mmol) at -78 °C. After being stirred for 30 min, the solution was warmed to the ambient temperature. The reaction mixture was evaporated, diluted with hexane (10 mL), and filtered. The filtrate was concentrated and the residue was subjected to revesed-phase column chromatography (20 mL) (R_f = 0.40-0.48) eluted with CH_3CN to give a mixture of **2** and **4**. The mixture was subjected to recycling reversed-phase liquid chromatogrphy to afford **2** (33 mg, 33% yield) and **4** (29 mg, 37% yield).

(3-Ethyl-1-penten-3-oxy)di(*p*-tolyl)chlorosilane. This compound was prepared from di(*p*-tolyl)dichlorosilane and 3-ethyl-1-penten-3-ol by essentially the same method as described in the literature.[4,9] This compound was subjected to distillation to be decomposed, so that it was used in the next step without purification. ^1H NMR (C_6D_6): δ 0.91 (t, J = 7.4 Hz, 6H), 1.72 (q, J = 7.4 Hz,

2H), 1.76 (q, J = 7.4 Hz, 2H), 2.08 (s, 6H), 5.10 (dd, J = 10.7 and 1.8 Hz, 1H), 5.37 (dd, J = 17.3 and 1.8 Hz, 1H), 5.81 (dd, J = 17.3 and 10.7, 1H), 7.05 (d, J = 7.6 Hz, 4H), 7.88 (d, J = 7.6 Hz, 4H).

[(3-Ethyl-1-penten-3-oxy)di(*p*-tolyl)silyl]trimethylstannane (7). This compound was prepared from (3-ethyl-1-penten-3-oxy)di(*p*-tolyl)chlorosilane and trimethylstannyllithium by essentially the same method as described for preparation of **2**. Purification was performed with reversed-phase column chromatography (R_f = 0.35) to give pure **7** as colorless oil (70% overall yield based on ditolyldichlorodisilane). ^{1}H NMR (C_6D_6): δ 0.38 (s, 9H), 0.89 (t, J = 7.4 Hz, 6H), 1.76 (q, J = 7.4 Hz, 4H), 2.12 (s, 6H), 5.11 (dd, J = 10.8 and 1.6 Hz, 1H), 5.33 (dd, J = 17.4 and 1.6 Hz, 1H), 5.85 (dd, J = 17.4 and 10.8 Hz, 1H), 7.11 (d, J = 7.6 Hz, 4H), 7.77 (d, J = 7.6 Hz, 4H). ^{13}C NMR (C_6D_6): δ -9.49, 8.56, 21.44, 32.45, 80.67, 114.25, 129.14, 135.00, 136.42, 139.49, 143.19. MS: *m/e* 488 (M^+, 0.9), 473 (M^+-Me, 2), 391 (13), 323 (M^+-$SnMe_3$, 57) 227 (100). Anal. Calcd for $C_{24}H_{36}OSiSn$: C, 59.15; H, 7.45. Found: C, 58.91; H, 7.54.

Crossover Experiment: Reaction of 2 and 7 with *n*-Butyllithium. To a solution of **2** (227 mg, 0.526 mmol) and **7** (267 mg, 0.548 mmol) in THF (3.0 mL) was added *n*-butyllithium in hexane (1.37 mL, 2.15 mmol) at -78 °C. After being stirred at -78 °C for 3 h, the solution was warmed to the ambient temperature and stirred for 2 h. To the solution was added trimethylchlorosilane (0.30 mL, 2.4 mmol). After being stirred for 30 min, the reaction mixture was evaporated, diluted with hexane (10 mL), and filtered. The filtrate was concentrated and the residue was subjected to column chromatography on silica gel (30 mL) eluted with hexane to give a mixture (324 mg, R_f = 0.3) of **4** (81% yield) and **8** (82% yield). ^{1}H NMR, GLC, and HPLC analyses of the reaction mixture showed that **9** and **10** were not formed at all. **1-(3'-Ethyl-2'-pentyl)-1,1-di(*p*-tolyl)-3,3,3-trimethyldisiloxane (8):** ^{1}H NMR (C_6D_6): δ 0.22 (s, 9H), 0.91 (t, J = 7.7 Hz, 3H), 1.03 (t, J = 7.4 Hz, 3H), 1.98-2.10 (m, 4H), 2.15 (s, 6H), 2.21 (d, J = 8.2 Hz, 2H), 5.45-5.54 (m, 1H), 7.13 (d, J = 7.8 Hz, 4H), 7.73 (d, J = 7.8 Hz, 4H). ^{13}C NMR ($CDCl_3$):

δ 2.02, 12.51, 12.99, 17.49, 21.53, 22.73, 29.26, 116.35, 128.36, 133.71, 134.32, 139.21, 141.71. MS: m/e 396 (M^+, 4), 381 (M^+-Me, 0.9), 299 ($Me_3SiO(Tol)_2Si^+$, 100), 207 (31), 193 (4). Anal. Calcd for $C_{24}H_{36}OSi_2$: C, 72.66; H, 9.15. Found: C, 72.76; H, 9.26.

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(6) For the formation of silyl anions from silylstannanes by treatment with higher order cuprates: Lipshutz, B. H.; Reuter, D. C.; Ellsworth, E. L. *J. Org. Chem.* **1989**, *54*, 4975.

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(8) In the presence of 12-crown-4, the tin-lithium exchange reaction appeared to be slow although the reason is not clear. No reaction occurred when **2** was treated with a 1 : 1 mixture of *n*-butyllithium and 12-crown-4 at −78 °C for 3 h.

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List of Publications

Part I

Chapter 1 — Tamao, K.; Kawachi, A.; Ito, Y. *J. Am. Chem. Soc.* **1992**, *114*, 3989.

Kawachi, A.; Tamao, K., to be submitted.

Chapter 2 — Tamao, K.; Kawachi, A.; Ito, Y. *Organometallics* **1993**, *12*, 580.

Chapter 3 — Tamao, K.; Kawachi, A.; Ito, Y., to be submitted.

Chapter 4 — Tamao, K.; Kawachi, A.; Tanaka, Y.; Ohtani, H.; Ito, Y., to be submitted.

Chapter 5 — Tamao, K.; Kawachi, A.; Nakagawa, Y.; Ito, Y. *J. Organomet. Chem.* **1994**, *473*, 29.

Part II

Chapter 6 — Tamao, K.; Kawachi, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 818.

Chapter 7 — Tamao, K.; Kawachi, A. *Organometallics* **1995**, *14*, 3108.

Chapter 8 — Kawachi, A.; Tamao, K., to be submitted.

Chapter 9 — Tamao, K.; Kawachi, A.; Doi, N., to be submitted.

Other Publications

(1) Tamao, K.; Kawachi, A.; Ito, Y. Xth International Symposium on Organosilicon Chemistry, August 15-20, 1993, Poznan, Poland, Proceedings, in press.

(2) Tamao, K.; Kawachi, A. *Ad. Organomet. Chem.* **1995**, *38*, 1.

(3) Tamao, K.; Sun, G-R.; Kawachi, A. *J. Chem. Soc., Chem, Commun*, **1995**, 2079.

(4) Tamao, K.; Sun, G-R.; Kawachi, A. *J. Am. Chem. Soc.* **1995**, *117*, 8043.

(5) Tamao, K.; Nagata, K.; Asahara, M.; Kawachi, A.; Ito, Y.; Shiro, M. *J. Am. Chem. Soc.* **1995**, in press.